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551 U.S. PTO



11/03/97

PTO/SB/13 (11-96)

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Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

REQUEST FOR FILING A PATENT APPLICATION UNDER 37 CFR 1.60

DOCKET NUMBER	ANTICIPATED CLASSIFICATION OF THIS APPLICATION		PRIOR APPLICATION EXAMINER	ART UNIT
	CLASS	SUBCLASS		
97-020	118	100+	08/407,191	1112

Address to:

Assistant Commissioner for Patents
Washington, D.C. 20231

This is a request for filing a ☐ continuation ☒ divisional application under 37 CFR 1.60, of pending prior Application Number 08/407,191, filed on 3/17/95 entitled Method and Apparatus for Controlled Placement of a Polymer Composition Into a Web

1. Enclosed is a copy of the latest inventor-signed prior application, including a copy of the oath or declaration showing the original signature or an indication it was signed. I hereby verify that the papers are a true copy of the latest signed prior application number 08/407,191, and further that all statements made herein of my own knowledge are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

CLAIMS	(1) FOR	(2) NUMBER FILED	(3) NUMBER EXTRA	(4) RATE	(5) CALCULATIONS
	TOTAL CLAIMS (37 CFR 1.16(c))	66 - 20 =	46	x \$ 22 =	\$ 1012
	INDEPENDENT CLAIMS (37 CFR 1.16(b))	3 - 3 =	0	x \$ 82 =	0
	MULTIPLE DEPENDENT CLAIMS (if applicable) (37 CFR 1.16(d))			+ \$ 0 =	0
				BASIC FEE (37 CFR 1.16(a))	+ 790
				Total of above Calculations =	1802
				Reduction by 50% for filing by small entity (Note 37 CFR 1.9, 1.27, 1.28).	(901)
				TOTAL =	\$901

2. ☒ A verified statement to establish small entity status under 37 CFR 1.9 and 1.27
☐ is enclosed.
☒ was filed in prior application number 08/407,191 and such status is still proper and desired (37 CFR 1.28(a)).
3. ☒ The Commissioner is hereby authorized to charge any fees which may be required under 37 CFR 1.16 and 1.17, or credit any overpayment to Deposit Account No. 14-0794. A duplicate copy of this sheet is enclosed.
4. ☐ A check in the amount of \$ _____ is enclosed.
5. ☒ Cancel in this application original claims 2-132 of the prior application before calculating the filing fee. (At least one original independent claim must be retained for filing purposes.)
6. ☒ The inventor(s) of the invention being claimed in this application is (are): James Michael Caldwell
7. ☐ This application is being filed by less than all the inventors named in the prior application. In accordance with 37 CFR 1.60(b), the Commissioner is requested to delete the name(s) of the following person or persons who are not inventors of the invention being claimed in this application:
8. ☐ Amend the specification by inserting before the first line the sentence: "This application is a ☐ continuation ☐ division of application number _____ / _____, filed _____, (status, abandoned, pending, etc.)."

[Page 1 of 2]

Burden Hour Statement: This form is estimated to take 0.5 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20231.

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(REQUEST FOR FILING A PATENT APPLICATION UNDER 37 CFR 1.60, PAGE 2)

9. ☒ New formal drawings are enclosed.
10. ☐ Priority of foreign application number _____, filed on _____ in _____
is claimed under 35 U.S.C. 119(a) - (d).
☐ The certified copy has been filed in prior application number ____ / _____, filed _____.
11. ☒ A preliminary amendment is enclosed.
12. ☒ The prior application is assigned of record to Nextec Applications, Inc.
13. ☒ Also enclosed: Power of Attorney and Petition to Accept Photographs
14. ☐ The power of attorney in the prior application is to: _____
- a. ☐ The power of attorney appears in the original papers in the prior application.
- b. ☐ Since the power does not appear in the original papers, a copy of the power in the prior application is enclosed.
- c. ☐ Address all future correspondence to: (May only be completed by applicant, or attorney or agent of record.)

☐ Customer Number

OR

Firm or

☒ Individual Name

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Country U.S.A.

Telephone (760) 438-5533

Fax (760) 438-5818

11/3/97
Date

Karl Stauss
Signature

Karl Stauss
Typed or printed name

- ☐ Inventor(s)
- ☐ Assignee of complete interest. Certification under 37 CFR 3.73(b) is enclosed.
- ☐ Attorney or agent of record
- ☒ Filed under 37 CFR 1.34(a)
Registration number if acting under 37 CFR 1.34(a). 40,827

A/\$
PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of: J. Michael Caldwell)
Serial No.: Unassigned)
Filed: November 3, 1997)
Title: Methods and Apparatus)
for Controlled Placement of)
a Polymer Composition Into)
a Web)
File No.: 97-020)

Examiner:

Art Unit:

**CERTIFICATE OF
"EXPRESS MAIL"**

Box NEW APP
Assistant Commissioner for Patents
Washington, D.C. 20231

Dear Assistant Commissioner:

CERTIFICATE OF "EXPRESS MAIL"

"Express Mail" mailing label number EG494071962US

I certify that this paper, along with:

Request for filing under 37 CFR § 1.60 form PTO/SB/13; Preliminary Amendment; Revocation and Appointment of New Power of Attorney; Formal drawings and Petition to accept photographs; Copy of originally filed U.S. Serial No. 08/407,191; and postcard;

are being deposited with the United States Postal Service as "Express Mail" in an envelope, under 37 C.F.R. § 1.10, on the date indicated below and is addressed to: Assistant Commissioner for Patents, Washington, D.C. 20231.

11/3/97
Date of Deposit

Deborah Watkins
Signature of Person Mailing Paper

Deborah Watkins
Name of Person Mailing Paper

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of: J. Michael Caldwell)
Serial No.: Unassigned)
Filed: November 3, 1997)
Title: Methods and Apparatus)
for Controlled Placement of)
a Polymer Composition Into)
a Web)
File No.: 97-020)

Examiner:

Art Unit:

**PRELIMINARY AMENDMENT
OF DIVISIONAL APPLICATION
FILED UNDER 37 CFR § 1.60**

Box NEW APP
Assistant Commissioner for Patents
Washington, D.C. 20231

Dear Assistant Commissioner:

Please enter the following preliminary amendment in the above identified application.

PRELIMINARY AMENDMENT

IN THE SPECIFICATION

In the **Cross-Reference to Related Patent Applications** section, please replace page 1, lines 4-9 with the following:

--This application is a division of U.S. Patent Application Serial No. 08/407,191 filed on March 17, 1995, status pending; which is a continuation-in-part of U.S. Patent Application Serial No. 08/017,855 filed on February 16, 1993, now U.S. Patent No. 5,418,051 issued May 23, 1995;

CERTIFICATE OF "EXPRESS MAIL"

"Express Mail" mailing label number EG494071962US

I certify that this paper, along with any referred to as being attached or enclosed, is being deposited with the United States Postal Service as "Express Mail" in an envelope, under 37 C.F.R. § 1.10, on the date indicated below and is addressed to: Assistant Commissioner for Patents, Washington, D.C. 20231.

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Deborah Watkins
Name of Person Mailing Paper

which is a continuation of U.S. Patent Application Serial No. 07/680,645 filed on April 2, 1991, now U.S. Patent No. 5,209,965 issued May 11, 1993; which is a continuation of U.S. Patent Application Serial No. 07/319,778 filed on March 10, 1989, now U.S. Patent No. 5,004,643, issued April 2, 1991; all of which are incorporated herein by reference.--

At page 32, line 2, please change "500" to --5,000--.

At page 53, line 11, please change "0.1" to --0.01--.

Please insert the following **Abstract**:

-- The present invention relates to an apparatus for controlling the placement of a curable, shear-thinnable polymer composition into a porous web. The apparatus comprises means for applying tension, means for applying the polymer composition to one surface of the tensioned web, and means for shear thinning the composition and placing it into the web to encapsulate at least some of the structural elements of the web, leaving most of the interstitial spaces open. A preferred apparatus includes one or more process heads that has mounted thereto a rigid knife blade for engagement with the web. The knife blade is movable vertically and rotationally. The process head is also movable horizontally along the path of the web. The invention also relates to an apparatus for selectively placing the polymer composition in a substantially continuous region extending through the web so that the polymer composition fills the interstitial spaces and adheres adjacent structural elements of the web in the region. In the areas of the web above and below the filled region, at least some of the structural elements are encapsulated and most of the interstitial spaces are open.--

IN THE CLAIMS

Please amend Claim 1 as follows:

1. (Amended) Apparatus for controlling the placement of a polymer composition into a porous web, having a three dimensional structure of a plurality of structural elements with interstitial spaces therebetween, comprising:

means for applying tension to the porous web;

means for applying a curable, shear-thinnable, polymer composition onto [a] one surface of the tensioned web; and

means for shear thinning the polymer composition to substantially reduce its viscosity and selectively [placing] place it into the tensioned web to encapsulate at least some of the structural elements, leaving [at least some] most of the interstitial spaces open.

Please add the following claims:

133. Apparatus for controlling the placement of a polymer composition into a porous web, having a three dimensional structure of a plurality of structural elements with interstitial spaces therebetween and a three dimensional top surface opposed from a three dimensional bottom surface, comprising:

means for applying tension to the web;

means for applying a curable, shear-thinnable, polymer composition onto one surface of the tensioned web;

blade means for engaging said one surface of the tensioned web;

means for moving the web relative to said blade means; and

means for controlling said tension applying means and said blade means to shear thin the polymer composition to substantially reduce its viscosity and to selectively place it into the tensioned web to encapsulate at least some of the structural elements, leaving most of the interstitial spaces open.

134. Apparatus as set in forth in Claim 1 wherein said shear thinning means selectively places said polymer composition to encapsulate most of the structural elements of said web.

135. Apparatus as set forth in Claim 1 wherein said polymer composition is selectively placed as an internal layer within said web positioned in a region extending through the web in a direction generally spaced from at least one major surface of said web; and

encapsulating at least some of the structural elements between said major surface and said region, leaving most of the interstitial spaces between said encapsulated structural elements open.

136. Apparatus as set in forth in Claim 1 wherein said shear thinning means selectively places said polymer composition, leaving substantially all of the interstitial spaces open.

137. Apparatus as set in forth in Claim 136 wherein said shear thinning means selectively places said polymer composition to encapsulate most of the structural elements of said web.

138. Apparatus as set in forth in Claim 136 wherein said shear thinning means selectively places said polymer composition to encapsulate substantially all of the structural elements of said web.

139. Apparatus as set forth in Claim 1 wherein:

said polymer composition is selectively placed to form a substantially continuous region extending through the web, said region of polymer composition filling the interstitial spaces and adhering adjacent structural elements;

said polymer composition is selectively placed to encapsulate at least some of the structural elements above and below said region; and

most of the interstitial spaces between said encapsulated structural elements above and below said region are open.

140. Apparatus as set forth in Claim 1 wherein the means for shear thinning comprises at least one blade forced against said one surface of the tensioned web;

said blade having a leading edge, a trailing edge, and a bottom surface.

141. Apparatus as set forth in Claim 140 wherein said leading and trailing edges are defined by adjacent surfaces having a finish of at least root mean square 8.

142. Apparatus as set forth in Claim 140 wherein the means for shear thinning comprises two or more blades spaced apart from one another.

143. Apparatus as set forth in Claim 140 wherein each blade extracts at least some of the polymer composition from the surface of the web and from within the web and reintroduces it into the web.

144. Apparatus as set forth in Claim 133 wherein said blade means also extracts polymer composition from the surface of the web and from within the web and reintroduces it into the web.

145. Apparatus as set forth in Claim 142 including means for controlling the spacing between said blades.

146. Apparatus as set forth in Claim 140 including means for separating the structural elements of the web.

147. Apparatus as set forth in Claim 146 wherein the means for separating comprises at least one nip stand.

148. Apparatus as set forth in Claim 140 wherein the blade is positioned perpendicularly to said moving web.

149. Apparatus as set forth in Claim 140 including means for independently varying the angle of the blade relative to said web.

150. Apparatus as set forth in Claim 140 including means for controlling the force of said blade relative to said web.

151. Apparatus as set forth in Claim 140 including means for moving the web relative to said blade.

152. Apparatus as set forth in Claim 151 including means for varying the exit angle of the moving web relative to said blade.

153. Apparatus as set forth in Claim 151 including means for varying the entrance angle of the moving web relative to said blade.

154. Apparatus as set forth in Claim 151 including means for varying both the entrance angle and the exit angle of said moving web relative to said blade.

155. Apparatus as set forth in Claim 142 including means for moving the web relative to said blades.

156. Apparatus as set forth in Claim 155 including means for varying the exit angle of the moving web relative to said blades.

157. Apparatus as set forth in Claim 155 including means for varying the entrance angle of the moving web relative to said blades.

158. Apparatus as set forth in Claim 155 including means for varying both the entrance angle and the exit angle of said moving web relative to said blades.

159. Apparatus as set forth in Claim 155 including means for independently controlling the force of each of said blades relative to said moving web.

160. Apparatus as set forth in Claim 1 including means for controlling the tension of the web.

161. Apparatus as set forth in Claim 1 wherein the shear thinning means also extracts polymer from the surface of the web and from within the web.

162. Apparatus as set forth in Claim 1 including means for curing the polymer composition within the porous web.

163. Apparatus as set forth in Claim 162 including means for controlling the temperature of the curing means.

164. Apparatus as set forth in Claim 162 wherein said curing means comprises a curing oven.

165. Apparatus as set forth in Claim 140 including means for controlling the temperature of said blade.

166. Apparatus as set forth in Claim 142 including means for controlling the temperature of each of said blades.

167. Apparatus as set forth in Claim 151 wherein said moving means comprises a pair of counter-rotating nip rolls.

168. Apparatus as set forth in Claim 167 including means for controlling the pressure between said nip rolls.

169. Apparatus as set forth in Claim 167 wherein one of the nip rolls has a rubber surface of a predetermined hardness.

170. Apparatus as set forth in Claim 167 wherein one of the nip rolls has a rubber surface of a predetermined hardness and one of the nip rolls has a metal surface of a predetermined hardness.

171. Apparatus as set forth in Claim 167 wherein both nip rolls have a rubber surface of predetermined hardness.

172. Apparatus as set forth in Claim 167 wherein both nip rolls have surfaces of different hardness or texture.

173. Apparatus as set forth in Claim 140 including means for damping the resonance of said blade.

174. Apparatus as set forth in Claim 142 including means for damping the resonance of said blades.

175. Apparatus as set forth in Claim 140 including means for vibrating said blade.

176. Apparatus as set forth in Claim 140 including means for vibrating said blade at a predetermined frequency.

177. Apparatus as set forth in Claim 142 including means for vibrating said blades.

178. Apparatus as set forth in Claim 142 including means for vibrating said blades individually at predetermined frequencies.

179. Apparatus as set forth in Claim 140 wherein said blade has a flat surface at the bottom thereof.

180. Apparatus as set forth in Claim 179 wherein the angle of entry of the web into said blade is greater than 0 degrees and less than 90 degrees, the web generally follows the bottom surface of said blade and the angle of exit of the web from said blade is greater than 0 degrees and less than 90 degrees.

181. Apparatus as set forth in Claim 1 including:
means for applying the polymer composition to the other surface of said web; and

means for shear thinning the polymer composition on said other surface to substantially reduce its viscosity and selectively place it into the tensioned web to encapsulate at least some of the structural elements, leaving most of the interstitial spaces open.

182. Apparatus as set forth in Claim 162 including means for controlling the release of tension of said web to cause the structural members to separate prior to cure.

183. Apparatus as set forth in Claim 162 wherein said web is under substantially no tension during curing.

184. Apparatus as set forth in Claim 162 including means for holding said web under transverse tension during curing.

185. Apparatus as set forth in Claim 1 including means for distorting the web during shear thinning to facilitate entrance of the polymer composition within the web.

186. Apparatus as set forth in Claim 185 wherein said means for distorting comprises means for stretching said web transversely.

187. Apparatus according to Claim 133 wherein said blade means comprises one or more additional blades for working the polymer composition into the web, extracting polymer composition from the surface of the web and from within the web, and reintroducing the polymer into the web.

188. Apparatus for controlled placement of a polymer composition into a porous web, having a three dimensional structure of a plurality of structural elements with interstitial spaces therebetween, comprising:

means for advancing a porous web;

means for applying tension to the porous web;

means for applying a curable, shear-thinnable, polymer composition to the web; and

means for shear thinning the polymer composition to reduce its viscosity and place it to encapsulate at least some of the structural elements, leaving most of the interstitial spaces open;

means for controlling the tension of the porous web during shear thinning of said polymer composition into said web; and

means for curing the polymer composition within the porous web.

189. Apparatus as set forth in Claim 188 including means for extracting the polymer composition from the surface of the web and from within the web.

190. Apparatus as set forth in Claim 188 wherein tension on the web is substantially released immediately prior to and during curing.

191. Apparatus as set forth in Claim 133 wherein tension on the web is substantially released immediately prior to and during curing.

192. Apparatus as set forth in Claim 133 wherein said means for controlling places said polymer to form a substantially continuous region extending through the web.

193. Apparatus as set forth in Claim 135 wherein said polymer composition includes an additive and at least some of said additive is placed on the surface of the encapsulated structural elements and at least some of said additive is placed on one or both surfaces of the internal layer.

194. Apparatus as set forth in Claim 139 wherein said polymer composition includes an additive and at least some of said additive is placed on the surface of the encapsulated structural elements and at least some of said additive is placed on one or both surfaces of the polymer region.

195. Apparatus as set forth in Claim 1 wherein said polymer composition includes an additive and at least some of said additive is selectively placed on one or both surfaces of said web.

196. Apparatus as set forth in Claim 1 including means for separating the structural elements of the web.


197. Apparatus as set forth in Claim 133 including means for separating the structural elements of the web.

REMARKS

This preliminary amendment is entered in order to file apparatus claims which were divided out of Applicant's previous U.S. Patent Application Serial No. 08/407,191. The new claims define an apparatus that encapsulates at least some of the structural elements of the web leaving most of the interstitial spaces between the encapsulated structural elements open. The new and amended claims are fully supported by the original specification and add no new matter. The changes made to the specification are fully supported by the specification at page 6, line 19 and page 30, line 21 and by the originally filed claims. No new matter has been added.

Respectfully submitted,

Dated: 11/3/97


Karl Stauss
Attorney for Applicant
Registration No. 40,827

Karl Stauss,
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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of:	J. Michael Caldwell)	
)	Examiner:
Serial No.:	Unassigned)	
)	Art Unit:
Filed:	November 3, 1997)	
)	
Title:	Methods and Apparatus)	PETITION TO ACCEPT
	for Controlled Placement of)	PHOTOGRAPHS UNDER
	a Polymer Composition Into)	37 CFR § 1.84(b)(1)
	a Web)	
)	
File No.:	97-020)	
)	

Box NEW APP
Assistant Commissioner for Patents
Washington, D.C. 20231

Dear Assistant Commissioner:

**SUBMISSION OF FORMAL DRAWINGS AND PETITION TO ACCEPT
PHOTOGRAPHS FILED UNDER 37 CFR § 1.84(b)(1)**

Applicant submits the enclosed formal drawings and respectfully petitions the
Commissioner to accept the enclosed black and white photographs.

CERTIFICATE OF "EXPRESS MAIL"

"Express Mail" mailing label number EG494071962US

I certify that this paper, along with any referred to as being attached or enclosed, is being deposited with the United States Postal Service as "Express Mail" in an envelope, under 37 C.F.R. § 1.10, on the date indicated below and is addressed to: Assistant Commissioner for Patents, Washington, D.C. 20231.

11/3/97
Date of Deposit

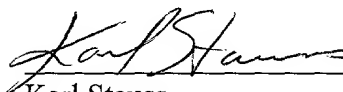
Deborah Watkins
Signature of Person Mailing Paper

Deborah Watkins
Name of Person Mailing Paper

Three (3) sets of photographs in accordance with 37 CFR § 1.84(b) are enclosed herewith. Please charge the petition fee of \$130.00 to Applicant's Deposit Account No. 14-0794.

Respectfully submitted,

Dated: 11/3/97



Karl Stauss
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**METHODS AND APPARATUS FOR CONTROLLED PLACEMENT OF A
POLYMER COMPOSITION INTO A WEB**

Cross-Reference to Related Patent Applications

This application is a continuation-in-part of U.S. Patent Application Serial No. 08/017,855 filed on February 16, 1993, now U.S. Patent No. 5,418,051 issued May 23, 1995; which was a continuation of U.S. Patent Application Serial No. 07/680,645 filed on April 2, 1991, now U.S. Patent No. 5,209,965 issued May 11, 1993; which was a continuation of U.S. Patent Application Serial No. 07/319,778 filed on March 10, 1989, now U.S. Patent No. 5,004,643, issued April 2, 1991; which was a continuation in part of U.S. Patent Application Serial Nos. 167,630; 167,643; 167,797; and 167,869 all filed on March 14, 1988; and all incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. *Field of the Invention*

The present invention relates to methods of and apparatus for the introduction of sufficient energy to controllably and selectively place a polymer composition into a porous web. The present invention more particularly relates to methods of and apparatus for the controlled placement of a curable, shear thinning, polymer composition into a web. The controlled placement is preferably performed through the energy controlled viscosity and rheology modified placement of the polymer controlled manner by 1) applying the polymer composition onto a surface of a web, 2) shear thinning the composition and placing it into the web, and 3) curing the polymer composition. This method and apparatus produces a web that either has some of its fibers or structural elements encapsulated by the polymer composition while at least some of the interstitial spaces of the web are open; or has an internal layer extending through the web in a direction generally spaced from at least one major surface thereof; or has both encapsulated structural elements and an internal layer of polymer composition.

2. *Description of Related Art*

In the prior art, it has been proposed to treat porous webs, especially fabrics, with silicone resins and also with fluorochemicals. Conventional treatments of webs fall into the general categories of (i) surface coatings and (ii) saturations or impregnations.

For example, U.S. Patent Nos. 3,436,366; 3,639,155; 4,472,470; 4,500,584; and 4,666,765 disclose silicone coated fabrics. Silicone coatings are known to exhibit relative inertness to extreme temperatures of both heat and cold and to be relatively resistant to ozone and ultraviolet light. Also, a silicone coating can selectively exhibit strength enhancement, flame retardancy and/or resistance to soiling. Fluorochemical treatment of webs is known to impart properties, such as soil resistance, grease resistance, and the like.

Prior art fluorochemical and silicone fabric treatment evidently can protect only that side of the fabric upon which they are disposed. Such treatments significantly alter the hand, or tactile feel, of the treated side. Prior silicone

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fabric coatings typically degrade the tactile finish, or hand, of the fabric and give the coated fabric side a rubberized finish which is not appealing for many fabric uses, particularly garments.

U.S. Patent No. 4,454,191 describes a waterproof and moisture-conducting fabric coated with a hydrophilic polymer. The polymer is a compressed foam of an acrylic resin modified with polyvinyl chloride or polyurethane and serves as a sort of "sponge", soaking up excess moisture vapor. Other microporous polymeric coatings have been used in prior art attempts to make a garment breathable, yet waterproof.

Various polyorganosiloxane compositions are taught in the prior art that can be used for making coatings that impart water-repellency to fabrics. Typical of such teachings is the process described in U.S. Patent No. 4,370,365 which describes a water repellent agent comprising, in addition to an organohydrogenpolysiloxane, either one or a combination of linear organopolysiloxanes containing alkene groups, and a resinous organopolysiloxane containing tetrafunctional and monofunctional siloxane units. The resultant mixture is catalyzed for curing and dispersed into an aqueous emulsion. The fabric is dipped in the emulsion and heated. The resultant product is said to have a good "hand" and to possess waterproofness.

This type of treatment for rendering fabrics water repellent without affecting their "feel" is common and well known in the art. However, it has not been shown that polyorganosiloxanes have been coated on fabrics in such a way that both high levels of resistance to water by the fibers/filaments and high levels of permeability to water vapor are achieved. As used herein, the term "high levels of permeability to water vapor" has reference to a value of at least about 500 gms/ m²/day, as measured by ASTM E96-80B. Also, as used herein, the term "high level of waterproofness" is defined by selective testing methodologies discussed later in this specification. These methodologies particularly deal with water resistance of fabrics and their component fibers.

Porous webs have been further shown to be surface coated in, for example, U.S. Patent Nos. 4,478,895; 4,112,179; 4,297,265; 2,893,962; 4,504,549; 3,360,394; 4,293,611; 4,472,470; and 4,666,765. These surface coatings impart various characteristics to the surface of a web, but do not substantially impregnate the web fibers. Such coatings remain on the surface and do not provide a film over the individual internal fibers and/or yarn bundles of the web. In addition, such coatings on the web surface tend to wash away quickly.

Prior art treatments of webs by saturation or impregnation also suffer from limitations. Saturation, such as accomplished by padbath immersion, or the like, is capable of producing variable concentrations of a given saturant chemical.

To treat a flexible web, by heavy saturation or impregnation with a polymer material, such as a silicone resin, the prior art has suggested immersion of the flexible web, or fabric, in a padbath, or the like, using a low viscosity liquid silicone resin so that the low viscosity liquid can flow readily into, and be adsorbed or absorbed

therewithin. The silicone resin treated product is typically a rubberized web, or fabric, that is very heavily impregnated with silicone. Such a treated web is substantially devoid of its original tactile and visual properties, and instead has the characteristic rubbery properties of a cured silicone polymer.

U.S. Patent No. 2,673,823 teaches impregnating a polymer into the interstices of a fabric and thus fully filling
5 the interstices. This patent provides no control of the saturation of the fabric. It teaches full saturation of the interstices of the fabric.

The prior art application of liquid or paste compositions to textiles for purposes of saturation and/or impregnation is typically accomplished by an immersion process. Particularly for flexible webs, including fabric, an immersion application of a liquid or paste composition to the web is achieved, for example, by the so-called padding process
10 wherein a fabric material is passed first through a bath and subsequently through squeeze rollers in the process sometimes called single-dip, single-nip padding. Alternatively, for example, the fabric can be passed between squeeze rollers, the bottom one of which carries the liquid or paste composition in a process sometimes called double-dip or double-nip padding.

Prior art treatment of webs that force a composition into the spaces of the web while maintaining some
15 breathability have relied on using low viscosity compositions or solvents to aid in the flow of the composition. U.S. Patent No. 3,594,213 describes a process for impregnating or coating fabrics with liquified compositions to create a breathable fabric. This patent imparts no energy into the composition to liquify it while forcing it into the spaces of the web. The composition is substantially liquified before placement onto and into the web. U.S. Patent No. 4,588,614 teaches a method for incorporating an active agent into a porous substrate. This patent
20 utilizes a solvent to aid in the incorporation of the active agent into the web.

Prior art apparatus for the coating of webs, including fabrics, generally deposits a coating onto the fabric at a desired thickness. Coating at a predetermined thickness can be achieved by deposition of coating material or by the scraping of a coating upon the fabric by knives. Flexible webs are generally urged between oppositely disposed surfaces, one of which would be a doctoring blade or drag knife. The blade or knife smooth the coating
25 and maintain the thickness of the coating to a desired thickness. For example, it is possible to apply a relatively thick silicone liquid elastomer coating to a rough web, typically of fiberglass, in order to make architectural fabric as is taught in U.S. Patent No. 4,666,765. In this example, the drag knives are set to a thickness of about 2 to 10 mils thicker than the web thickness. This setting, depending on the coating speed, can yield a base coat thickness of approximately 3 to 12 mils thicker than the web thickness.

30 Various types of coatings, and various coating thicknesses, are possible. However, a general principle of coating machinery is that the coating material is swept, or dragged, along the surface of the fabric. No special attention is normally given to any pressured forcing of the coating into the fabric, therein making the coating also serve as

an impregnant. Of course, some coating will be urged into surface regions of the fabric by the coating process. Generally, however, application of high transversely exerted (against a fiber or web surface) forces at the location of the coating deposition and/or smoothing is not desired in the prior art processes because it is the goal of the prior art coating processes to leave a definite thickness of coating material upon a surface of the fabric, and not to scrape the fabric clean of surface-located coating material.

One prior art silicone resin composition is taught by U.S. Patent Nos. 4,472,470 and 4,500,584, and includes a vinyl terminated polysiloxane, typically one having a viscosity of up to about 2,000,000 centipoises at 25°C, and a resinous organosiloxane polymer. The composition further includes a platinum catalyst, and an organohydrogenpolysiloxane crosslinking agent, and is typically liquid. Such composition is curable at temperatures ranging from room temperature to 100°C or higher depending upon such variables as the amount of platinum catalyst present in the composition, and the time and the temperature allowed for curing.

Such compositions may additionally include fillers, including finely divided inorganic fillers. Silicone resin compositions that are free of any fillers are generally transparent or translucent, whereas silicone resin compositions containing fillers are translucent or opaque depending upon the particular filler employed. Cured silicone resin compositions are variously more resinous, or hard, dependent upon such variables as the ratio of resinous copolymer to vinyl terminated polysiloxane, the viscosity of the polysiloxane, and the like.

Curing (including polymerization and controlled crosslinking) can encompass the same reactions. However, in the fabric finishing arts, such terms can be used to identify different phenomena. Thus, controllable and controlled curing, which is taught by the prior art, may not be the same as control of crosslinking. In the fabric finishing arts, curing is a process by which resins or plastics are set in or on textile materials, usually by heating. Controlled crosslinking may be considered to be a separate chemical reaction from curing in the fabric finishing arts. Controlled crosslinking can occur between substances that are already cured. Controlled crosslinking can stabilize fibers, such as cellulosic fibers through chemical reaction with certain compounds applied thereto. Controlled crosslinking can improve mechanical factors such as wrinkle performance and can significantly improve and control the hand and drape of the web. Polymerization can refer to polymer formation or polymer growth.

SUMMARY OF THE INVENTION

The present invention includes methods and apparatus for controlling a porous web under tension, for applying a curable or semi-curable, shear thinnable polymer composition onto the surface of the web, for shear thinning the polymer composition, and placing it into the web to position the polymer within the web in a certain manner, and for partially or fully curing the polymer composition. The methods and apparatus of this invention control the placement of the composition into the web to either encapsulate the structural elements (i.e., the fibers or

filaments) making up the web leaving at least some of the interstitial spaces open or providing an internal layer of polymer between the upper and lower surfaces of the web, or some combination of the foregoing.

The methods and apparatus of the present invention permits the application of the polymeric composition onto the surface of the web by a variety of means. After the polymer is applied to the surface of the web, the polymer composition is preferably immediately shear thinned to controllably and significantly reduce its viscosity and place it into selected places within the web. To aid in this process, the web is preferably distorted, typically by stretching at the location of the shear thinning. This distortion facilitates the entrance of the polymer composition into the web by creating a double or dual shear thinning. In the case of the web, this is produced by the combination of the edge condition of the blade, the engineered shear thinnable polymer, the speed of the web, and the subsequent repositioning of the fibers and filaments after their immediate passage under the edge of the blade.

Controlled placement of the polymer composition within a web may be performed by a basic embodiment of a machine in accordance with the present invention, that is as simple as an applicator to apply viscous polymer to the surface of the web, a pair of facilities for applying tension to a section of the web and a blade forced against the web in the section under tension. The web is pulled under tension past the blade, or, alternatively, the blade is moved relative to the web, and the forces generated by the blade cause the polymer composition to flow into the three-dimensional matrix of the web, and controllably be extracted out of the web leaving a thin film of polymer encapsulating selected fibers, or an internal layer of polymer, or both. Tension on the web is preferably released thereafter, and the web is cured.

The present invention includes novel methods and apparatus for manufacturing webs, fibers and fabrics that have certain desirable physical qualities such as water resistance, increased durability, and improved barrier qualities by combining the use of encapsulated fibers and filaments and a breathable or controlled pore size internal coating with a controlled surface chemistry modification and the like. Such webs, fibers and fabrics can be used to prepare a wide variety of products including, but not limited to, carpets, specialized clothing, career apparel, bioengineered surfaces for diagnostic applications, and upholstery. By use of the present invention, webs, fibers and fabrics can be manufactured with a wide variety of desired physical characteristics.

Methods and apparatus of the present invention can treat webs or fabrics which are generally flat or planar with great internal precision of the internal placement, by combining the use of encapsulated fibers and filaments and a breathable or controlled pore size internal layer, with a controlled surface chemistry modification. Surface chemistry is controlled by using sufficient web tension and frontal blade energy to dislodge the fluorochemical from the web which is then caused to surface orient and/or bloom. The webs or fabrics can comprise fibers in the form of monofilaments, yarns, staples, or the like. The webs or fabrics can also be comprised of a matrix having open cells or pores therein. The webs or fabrics may be a fabric which is woven or non-woven with fibers

that can be of any desired composition. The webs or fabrics will generally be tensionable, but not too weak or elastomeric to be processed in accordance with the teachings of the present invention. Any web that is too weak or elastomeric can be treated in accordance with the subject invention if it is laminated to a support backing of paper, film, such as Mylar, or the like and controllably stretched or not stretched prior to applying the backing, thereby setting the condition under which it is stabilized so that it can be treated in accordance with this invention.

The methods and apparatus of this invention are also applicable to treating discrete sheets or pieces of webs such as papers, film sheets, foam sheets, leather hides, woven and non-woven sheets, and the like. The sheet is fed into the apparatus and stops. It is placed under tension and polymer is applied. Rigid or non-rigid blades are moved across the surface of the sheet to cause the controlled placement of the polymer within the sheet as previously described. A non-rigid blade can be flexible but must have sufficient shearing capability.

Webs treated by the methods and apparatus of the present invention contain a curable or semi-curable polymer or copolymer that may contain monomers that are present as a film, coating, or layer within a web that envelopes or encapsulates at least a portion of the fibers or cell or pore walls of the web. The internal layer is a region generally spaced from the outer surfaces of the web which is substantially continuously filled by the combination of the polymers controllably placed therein and the fibers and filaments of the web in this region. The interstices or open cells in the region of the internal layer are also substantially filled. The outer surfaces of the web are substantially free of any polymer deposits other than the thin film encapsulation of the surface fibers and filaments. However, the web remains breathable and is either water resistant or waterproof. The thickness of the internal layer is generally in the range of 0.01 to 50 microns.

At a microscopic level, a web treated in accordance with the present invention, for example, a fabric, can be regarded as being a complex structure, but generally the internal layer is discernable under microscopic examination as shown in the accompanying scanning electron microscope photographs that will be discussed hereinafter.

Depending upon the conditions used to produce it, a web produced in accordance with the present invention can characteristically and preferably exhibit a soft hand and flexibility that is comparable to the hand and flexibility of the untreated web. In some cases, the difference between the hand and the feel of the treated and untreated webs may not be perceptible, but may be engineered to be altered through the controlled crosslinking of the polymer. This is particularly surprising in view of the substantial amount of polymer being added to the web. A treated web has a breathability which, by a present preference, can approach a high percentage of the untreated web notwithstanding the relatively large amount of polymer present.

A polymer composition having a viscosity in the range of greater than 1,000 centepoise but less than 2,000,000 centepoise is preferably used to produce the treated webs. If desired, additives or modifiers can be admixed with

such a composition to adjust and improve properties of such composition or web, such as viscosity and/or rheology, combustibility, reflectivity, flexibility, conductivity, light fastness, mildew resistance, rot resistance, stain resistance, grease resistance, and the like. In general, a web treated in accordance with this invention exhibits enhanced durability. These additives are generally controlled by the engineered shear thinning polymer composition and the method and apparatus of this invention to be oriented and surface exposed on the surface of the thin film on the encapsulated fibers, or on one or both surfaces of the internal layer, or on one or both surfaces of the web, or some combination of the above.

A web made by the present invention can preserve much, or even substantially all, of its original untreated hand even after an extended period of use while demonstrating excellent abrasion resistance. In contrast, an untreated web typically loses its original hand and displays reduced abrasion resistance after an extended period of use. This is achieved by the formation of an internal layer that prevents new fiber surfaces from being exposed, thereby minimizing the amount of untreated surfaces that degrade much faster than the treated fibers.

A web treated by this invention can undergo a large number of machine washings with detergent without experiencing appreciable or significant change or deterioration. The polymer matrix composition prolongs the use and service life of a web, usually by at least an order of magnitude, depending on such factors as web type, extent and type of treatment by the teachings of this invention, and the like.

Optionally, and as indicated above, agents or additives carried by the polymer composition into a web can be stably fixed and selectively placed in the web with the cured polymer. For example, agents such as ultraviolet light absorbers, dulling agents, reflectivity enhancers, antimicrobial agents, flame resistant agents, heat absorbant, anti-static agents, and the like, which modify a web's response to light and radiation are desirably located substantially upon the surfaces of the web's fibers. When these agents are incorporated into the enveloping polymer film, it appears that they are retained where they are deposited. A present preference for ultraviolet resistant webs in the practice of this invention is to employ a silicone polymer composition that contains a benzophenone.

In addition, the present invention is directed to methods and apparatus for making polymer encapsulated and internally coated webs. Such methods and apparatus includes means for tensioning a porous, flexible web; means for applying a curable, shear thinnable, polymer composition thereto; and means for applying a localized shear force sufficient to cause the controlled shear thinning of an engineered polymer over and against one or both surfaces of the tensioned web. The shear force is sufficient to shear thin the polymer, to selectively distribute and place the polymer composition within the web as an internal layer in a region extending generally in spaced relationship to the surfaces of the web and to generally envelop surface portions of at least some of the web fibers or form a lining of the cells or pores of the web. The internal layer is not necessarily flat but may undulate or meander through the web, occasionally even touching one or both surfaces of the web. Alternatively, the shear

force and other variables are controlled to encapsulate at least some of the internal and external fibers of the web without forming an internal layer. Also, control of the methods and apparatus can result in a treated web having a combination of an internal layer and encapsulation of at least some of the fibers of the web leaving at least some of the interstitial spaces open. The web is then optionally interveningly stored, or is (preferably) immediately subjected to curing conditions (heat, moisture and/or radiation) which converts the polymer composition as deposited in the web into a solid elastomeric polymer. The web can be semi-cured or partially cured and can be finally cured or post cured at a later time.

Various other and further features, embodiments, and the like which are associated with the present invention will become apparent and better understood to those skilled in the art from the present description considered in conjunction with the accompanying drawings wherein presently preferred embodiments of the invention are illustrated by way of example. It is to be expressly understood, however, that the drawings and the associated accompanying portions of this specification are provided for purposes of illustration and description only, and are not intended as limitations on the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graphical plot illustrating the flow of a silicone polymer composition over time upon and in fabrics both pretreated and untreated with water repellent chemicals, such as fluorochemicals.

Figure 2 is a plan view of a prior art silicone polymer treated fabric magnified 150 times.

Figure 3a is a photomicrograph of a fabric of the invention magnified 120 times.

Figure 3b is a cross section of a fiber bundle fabric of Figure 3a magnified 600 times.

Figure 3c is a view of the side of the fabric of Figure 3a that is the opposite of the side to which silicone polymer was applied.

Figures 4a and 4b illustrate diagrammatically one embodiment of a method and apparatus suitable for use in the practice of the present invention.

Figure 5 is a diagrammatic representation illustrating the process in accordance with the present invention.

Figure 6 illustrates diagrammatically another embodiment of a methods and apparatus suitable for use in the practice of the present invention.

Figure 7 illustrates diagrammatically another embodiment of a method and apparatus suitable for use in the practice of the present invention.

Figures 8a through 8d are graphs illustrating ways of plotting rheological behavior.

Figure 9 is a schematic vector diagram illustrating surface tension forces.

5 Figure 10 is a graph relating contact angle over a smooth, solid surface.

Figures 11a through 11d show representative velocity profiles.

Figures 12a through 12c illustrate diagrammatically other methods and apparatus suitable for use in the practice of the present invention.

10 Figures 13a through 13c are scanning electron microscope photomicrographs of another representative fabric made in accordance with of the present invention.

Figure 14 illustrates diagrammatically another and presently preferred embodiment of methods and apparatus suitable for use in the practice of the present invention.

Figures 15a through 15i are scanning electron microscopy (SEM) photomicrographs and elemental analyses which depict various results in fabrics, fibers and filaments from back scatter evaluation tests.

15 **DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The following description is of the best presently contemplated mode of carrying out the invention. This description is made for the purpose of illustrating the general principles of the inventions and should not be taken in a limiting sense.

20 The present invention relates to methods and apparatus for manufacturing a treated web. The subject methods and apparatus involve the control of numerous variables, including, without limitation, web tension (both overall web tension as well as the web tension immediately before and after each individual blade), angle of entry of web into each blade, blade angle in relation to horizontal reference point, blade pressure against moving web, angle of exit of web from each blade, web speed, number of blades, the pressure of the leading nip rolls, the pressure of the trailing nip rolls, static control, thickness of each blade, bevel on each blade, oven cure temperature, oven
25 cure dwell time, blade temperature and blade surfaces and edge conditions and blade finish.

Other variables that affect the finished product, but are not directly related to the methods and apparatus, include, without limitation, the polymer blend, the starting viscosity of the polymer composition, accelerators added to the polymer composition, additives added to the polymer composition, the type of web used, ambient temperature, humidity, airborne contaminants, lint on web, pre-treatment of web, sub-web surface temperature, and web moisture content.

With respect to the blades, the temperature of the blade can be kept cool to keep the polymer composition from curing prematurely. This can be accomplished by passing a coolant through or around the blade or by other means well known in the art. Alternatively, the blade could be heated by passing a heated fluid around or through the blade, if desired to improve or alter the viscosity and rheology for the required changes in the polymer necessary to achieve a specific product.

The blade finish is also important. A hard, smooth surface of both blade face and edges is desirable to shear thin the polymer and keep it flowing and to maximize friction or selectively create shear forces between the web, the polymer, and blade(s). For some applications, the blades should preferably remain rigid in all dimensions and have minimal resonance in order to get uniform web treatment.

The apparatus has facilities for rotating the angle of each blade $\pm 90^\circ$ from the vertical. In order to vary the shear and placement forces of the blade against the web, polymer and additives, adjustment facilities are provided for moving the blade vertically up and down and moving the blade forward and backward horizontally. All three axis are important for creating the desired control which causes the encapsulated fibers and/or filaments, the additive placement and orientation on the fiber and filaments, the optional internal layer, and the controlled thickness of the encapsulating films or internal layer. The lateral placement of each blade relative to the other is also important and facilities are provided for allowing lateral movement of each blade toward and away from each other. The lateral placement of each blade controls the micro tension and elastic vibration of the web between the preceding roll and the blade, thereby controlling the web after the immediate exit of the web from the blade and controlling the Coanda Effect, as described in U.S. Patent 4,539,930, so that controlled placement of the internal layer takes place.

Changing the tension of the web results in changes internally in the web, such as the position of the internal layer of the web, as well as how much or how little fiber encapsulation occurs, and the thickness of the film encapsulating the individual fibers or filaments.

At the leading edge of the blade, the web is stretched longitudinally and the polymer is simultaneously and dynamically shear thinned, placed into the web, and partially extracted from the web, thereby leaving encapsulated fibers and filaments and/or an internal layer. As the web passes the leading edge of the blade, the elastic recovery forces of the web combined with the relaxation or elastic recovery of the fibers and filaments

causes fiber encapsulation and the surface chemistry modification (or bloom). It is believed that this occurs by the popping apart of the individual fibers and filaments. The fibers and filaments either pull the polymer from the interstitial spaces or the rheology of the polymer attracts it to the fibers and filaments or some combination of the two. The end result is that the polymer in the interstitial spaces moves to the fibers and filaments as they move or snap apart, thereby creating encapsulated fibers and filaments. At the bottom surface of the blade, the thickness, depth, and controlled placement of the internal layer is determined. A wider blade results in a thicker internal layer of polymer. Further, the dynamics of stretch and relaxation of the fibers provides for an even energy necessary for the thin film encapsulation of the polymer composition over the fibers.

Passing the treated web through the exit nip rolls pushes the fibers or structural elements of the web together.

The hardness of and the material of the exit nip rolls affects the finished web. The exit nip rolls could be either two rubber rolls or two steel rolls, or one steel roll and one rubber roll, and the rubber rolls could be of different durometers. Further, the variation of the hardness of one or both nip rolls changes the contact area or footprint between the nip rolls and the web as the web passes therebetween. With a softer roll there is a larger contact area and the web is capable of retaining the (a) thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal coating, and (c) controlled placement of the additives in (a) and (b). With a harder roll there is a smaller contact area which is appropriate for heavier webs.

Additional controllable variables include the various controls of each blade, the nip rolls durometer, the nip release effect, the nip surface characteristics, the guidance, and the pre-treatment of the substrate. Some of the controllable variables are: 1) web tension, 2) angle of entry of fabric into the blade, 3) blade angle in reference to horizontal position, 4) blade pressure against fabric (blade height), 5) angle of exit of fabric from blade, 6) web speed, 7) number of blades, 8) initial rheology and viscosity of polymers, 9) nip pressure, 10) entry nip pressure, 11) static control, 12) blade thickness and shape, 13) polymers and polymer blends, 14) accelerators and inhibitors added to polymers, 15) additives in polymers, 16) oven cure temperature, 17) oven cure dwell time, 18) substrate type, 19) ambient polymer temperature, 20) humidity, 21) degree web is deformed under lateral tension, and 22) airborne contaminants and lint on the web. Control of the above variables affects: (a) the thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal coating, and (c) the controlled placement of the additives in (a) and (b).

An increase in web tension causes less polymer to be applied to the web, and also, more of what is applied to be extracted from the web. Web tension occurs between the entrance pull stand and the exit pull stand. The primary tension is a result of the differential rate between the driven entrance pull stand and the driven exit pull stand whereby the exit pull stand is driven at a rate faster than the entrance pull stand. Other factors which effect tension are (1) the blade roll diameter, (2) the vertical depth of the blade(s), (3) the durometer of the entrance pull stand roll and rubber roll of the exit pull stand, and (4) the friction as the web passes under the blade(s). The larger the blade roll diameter, the higher the tension of the web. If the drive rate of the web remains constant, then

increasing the depth of the blade into the web creates a greater micro tension condition under the blade. Similarly, decreasing the depth into the web decreases the micro tension under the blade. The lower the durometer of the entrance pull stand roll and rubber roll of the exit pull stand, the larger the footprint or contact area between the rolls. A larger footprint produces more surface friction, thereby limiting web slippage and increasing tension.

- 5 Likewise, web slippage can be effected by changing the surface texture of the rolls, i.e., a smooth roll will allow greater slippage than a highly contrasting or rough surface texture. Increasing friction, as the fabric passes under the blade(s), also produces tension. Friction is a function of the surface area of the bottom of the blade(s). Increasing the surface area increases the friction which increases the tension.

- 10 The entry angle of the web into the blade(s) can be varied by blade roll height, blade roll diameter, blade angle, distance between prior blade roll(s) and blade(s), and height of the blades. Increasing the blade roll height and blade roll diameter increases the entry angle into the blade. Rotating the blade angle clockwise from the perpendicular, with the web running left to right, increases the entry angle. Likewise, rotating the blade angle counter-clockwise from the perpendicular, with the web running left to right, decreases the entry angle. Decreasing the distance between the roll before the blade and the blade decreases the angle of entry. Increasing
15 the downward depth of the blade(s) into the web decreases the angle of entry into the blade(s).

The angle of the blade(s) is completely changeable and fully rotational to 360°. The fully rotational axis provides an opportunity for more than one blade per rotational axis. Therefore, a second blade having a different thickness, bevel, shape, resonance, texture, or material can be mounted. Ideally the apparatus contains two or three blades per blade mount.

- 20 The blade height or blade pressure applied against a web can be obtained through the vertical positioning of the blade(s) in the blade mount. The greater the downward depth of the blade(s), the greater the pressure. Blade pressure against the web is also accomplished through the tension of the web as described above.

- The same line components that affect the entry angle of the web into the blade(s), also affect the exit angle of the web out of the blade. Any changes in blade roll(s) vertical height, diameter, or distance away from the blade,
25 affects the exit angle of the web. If the angle of the blade is rotated clockwise as described above, the entry angle of the web increases, thus decreasing the exit angle.

Web speed is proportional to the variable speed of the motor which drives the entrance and exit nip stands. Web speed can effect the physics of the polymers as the web passes under the blades.

- 30 The number of blades can vary. Generally, more than one blade is required. The polymer is first applied onto the web prior to the first blade. At this blade, a rolling bead of polymer can exist at the interface of the blade and

the web (entry angle) Basically, a high viscosity polymer is applied and through the process of shear thinning, the viscosity is greatly decreased, allowing the polymer to enter into the interstitial spaces of the web. Any blade(s) after the first blade, serves to further control the polymer rheology and viscosity and continue the controlled placement of the polymer into the web. This is accomplished by controllably removing excess polymer to obtain an even distribution of polymer to any area, or a combination of the three areas of a) the thin film encapsulation of the individual fibers and filaments, b) the controlled placement of the internal layer, and c) the controlled placement of the additives in a) and b).

The initial process dynamics for the rheology and viscosity of the polymer is designed and engineered with the required attributes to achieve (a) the thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal layer, and (c) the controlled placement of the additives in (a) and (b). If the polymer viscosity is high, the polymer may need to be pre-thinned by using a dynamic mixer or three-roll head, as shown in Figure 12a. The dynamic mixer or the three-roll head can significantly reduce the viscosity and even pre-place the polymer into a thick substrate or web to allow the blades to further shear thin and enhance the flow and placement of the polymer.

The entrance pull stand is a driven roll proportionally driven at a predetermined rate slower than the exit pull stand. The entrance and exit pull stands are adjustable from about 100 pounds of force to 5 or more tons of force.

The bottom rolls of both the entrance and exit pull stands have micro-positioning capability to provide for gap adjustment and alignment. The composition of the top roll of the entrance and exit pull stands is chosen based on the durometer of the urethane or rubber. The top roll of the exit pull stand preferably utilizes a Teflon sleeve which will not react with the polymers used in the process. The bottom roll of the exit pull stand is preferably chrome plated or highly polished steel to reduce the impression into the preplaced polymer in the web.

If desired, non-contact antistatic devices may be installed in locations where noticeable levels of static buildup are detected. However, there is no evidence of adverse effects due to static buildup in the process.

Blade thickness and shape have substantial effects on the movement of the structural elements of the web during processing and more importantly, the viscoelastic flow characteristics of the polymer in controlling (a) the thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal coating, and (c) the controlled placement of the additives in (a) and (b). The blade bevel can effect the entry angle of the web and effect the sharpness of the leading edge of the blade. A sharper leading edge has a greater ability to push the weave or structural elements of the web longitudinally and transversely, increasing the size of the interstitial spaces. As the web passes the leading edge of the blade, the interstitial spaces snap back or contract to their original size. The polymer viscosity is reduced and the polymer is placed into the web at the leading edge of the blade. Blade thickness and shape effects the polymers and their selected additives and the placement thereof. Preferably, the

combination of the leading edge condition and the two surfaces (the front and the bottom) that meet at the leading edge are RMS 8 or better in grind and/or polish. This creates a precise leading edge; the more precise the leading edge, the more the shear thinning control.

There are a number of pre-qualifiers or engineered attributes of polymers that enhance control of flow and polymer placement in: (a) the thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal coating, and (c) the controlled placement of the additives in (a) and (b). Blending polymers is one way to achieve ideal flow and placement characteristics. An example of a blended polymer is where one polymer, selected for its physical properties, is mixed with another polymer that is selected for its viscosity altering properties. Many tests using different polymer blends have been done. Polymer blends vary by both chemical and physical adhesion, durability, cure dwell time required, cure temperature required, flexibility, percentage add-on required, performance requirements, and aesthetics.

Accelerators and inhibitors which are added to polymers, generally produce three effects. An illustrative accelerator or inhibitor is a platinum catalyst, which is a cure or crosslinking enhancer. The first effect it produces is to control the time and temperature of the web as it cures. A cure or controlled crosslinking enhancer can significantly assist in controlling the drape and hand feel of the web. The second effect is to alter the cure to allow the web to reach partial cure and continue curing after leaving an initial heat zone. This second effect also assists in retaining the drape and hand feel of the web. The third effect of inhibitors is to achieve a semi-cure for later staging of the cure.

Additives which are added to the polymers significantly control surface chemistry. Surface chemistry characteristics are controlled by including additives that have both reactive and bio-interactive capabilities. The method and apparatus of this invention can control the placement of the additives on the surface of the thin film encapsulating the fibers, on either or both surfaces of the internal layer, on either or both surfaces of the web, or any combination of the foregoing.

The oven cure temperature and the source and type of cure energy, are controlled for a number of reasons. The oven cure temperature is controlled to achieve the desired crosslinked state; either partial or full. The source and type of energy can also affect the placement of the polymer and additives. For example, by using a high degree of specific infrared and some convection heat energy for cure, some additives can be staged to migrate and/or bloom to the polymer surfaces.

Oven cure temperature is thermostatically controlled to a predetermined temperature for the web and polymers used. Machine runs of new webs are first tested with hand pulls to determine adhesion, cure temperature, potentials of performance values, drapability, aesthetics, etc. The effect on the web depends on the oven temperature, dwell time and curing rate of the polymer. Webs may expand slightly from the heat.

Oven cure dwell time is the duration of the web in the oven. Oven cure dwell time is determined by the speed of the oven's conveyor and physical length of the oven. If the dwell time and temperature for a particular web is at maximum, then the oven conveyor speed would dictate the speed of the entire process line or the length of the oven would have to be extended in order to increase the dwell time to assure proper final curing of the web.

- 5 The physical construction and chemistry of the web is critical. The amount of control over the rheology of the polymer and the tension on the web are dependent on the physical construction and chemistry. The web selected must have physical characteristics that are compatible with the flow characteristics of the polymer.

The ambient polymer temperature refers to the starting or first staging point to controlling the viscosity and rheology. The process head can control the ambient polymer temperature through temperature controlled polymer delivery and controlled blade temperatures.

Humidity can sometimes inhibit or accelerate curing of the polymer. Therefore, humidity needs to be monitored and, in some conditions, controlled.

The degree the web is deformed under lateral tension is controllable by the choice of the physical construct of the web, the blade angle, the blade leading edge condition, and the micro and macro tension of the web.

- 15 Airborne contaminants and lint on the web can affect primability and can create pin holes in the polymer. Therefore, airborne contaminants and lint on the web need to be controlled to reduce or eliminate pin holes or uncontrolled primability.

In view of the fact that between the shear thinning stations and the oven, the polymer composition may begin to set or partially cure, it may be desirable to overshear so that by the time the web gets to the curing oven, it will be at the point where it is desired that the cure occur. This over shear effect is a matter of controlling certain variables, including the force of the blades against the moving web, as well as the tension and speed of the web.

By having a number of shear thinning blades, you create a multiple shear thinning effect, which changes the final construct of the polymer and the (a) thin film encapsulation of the individual fibers and filaments, (b) controlled placement of the internal coating, and (c) controlled placement of the additives in (a) and (b). It is understood that the first shear thinning causes viscoelastic deformation of the polymer composition which, due to its memory, tends to return to a certain level. With each multiple shear thinning, the level to which the polymer starts at that shear point and returns is changed. This is called thixotropic looping or plateauing.

Definitions

The term "web" as used herein is intended to include fabrics and refers to a sheet-like structure (woven or non-woven) comprised of fibers or structural elements. Included with the fibers can be non-fibrous elements, such as particulate fillers, binders, dyes, sizes and the like in amounts that do not substantially affect the porosity or flexibility of the web. While preferably, at least 50 weight percent of a web treated in accordance with the present invention is fibers, more preferred webs have at least about 85 weight percent of their structure as fiber. It is presently preferred that webs be untreated with any sizing agent, coating, or the like, except as taught herein. The web may comprise a laminated film or fabric and a woven or non-woven porous substrate. The web may also be a composite film or a film laminated to a porous substrate or a double layer.

- 10 The term "webs" includes flexible and non-flexible porous webs. Webs usable in the practice of this invention can be classified into two general types:

- (A) Fibrous webs; and
- (B) Substrates having open cells or pores, such as foams.

- 15 A porous, flexible fibrous web is comprised of a plurality of associated or interengaged fibers or structural elements having interstices or interstitial spaces defined therebetween. Preferred fibrous webs can include woven or non-woven fabrics. Other substrates include, but are not limited to, a matrix having open cells or pores therein such as foams or synthetic leathers.

- 20 The term "fiber", as used herein, refers to a long, pliable, cohesive, natural or man-made (synthetic) threadlike object, such as a monofilament, staple, filament, or the like. A fiber usable in this invention preferably has a length at least 100 times its diameter or width. Fibers can be regarded as being in the form of units which can be formed by known techniques into yarns or the like. Fibers can be formed by known techniques into woven or non-woven webs (especially fabrics) including weaving, knitting, braiding, felting, twisting, matting, needling, pressing, and the like. Preferably, fibers, such as those used for spinning, as into a yarn, or the like, have a length of at least about 5 millimeters. Fibers such as those derived from cellulose of the type produced in paper manufacture can be used in combination with longer fibers as above indicated, as those skilled in the art will readily appreciate.

The term "filament" as used herein refers to a fiber of indefinite length.

- 30 The term "yarn" as used herein refers to a continuous strand comprised of a multiplicity of fibers, filaments, or the like in a bundled form, such as may be suitable for knitting, weaving or otherwise used to form a fabric. Yarn can be made from a number of fibers that are twisted together (spun yarn) or a number of filaments that are laid

together without twist (a zero-twist yarn).

A flexible porous web used as a starting material in the present invention is generally and typically, essentially planar or flat and has generally opposed, parallel facing surfaces. Such a web is a three-dimensional structure comprised of a plurality of fibers with interstices therebetween or a matrix having open cells or pores therein.

- 5 The matrix can be comprised of polymeric solids including fibrous and non-fibrous elements.

Non-fibrous elements, such as particulate fillers, binders, dyes, sizes and the like can be added to fibers in a web. Preferred webs have at least about 85% of their structure comprised of fibrous or fiber materials and are untreated with any sizing agent, coating, or the like.

- Two principal classes of substrates having open pores or cells may be utilized in the present invention: leathers
10 (including natural leathers, and man-made or synthetic leathers), and foamed plastic sheets (or films) having open cells.

- Foamed plastic sheet or film substrates are produced either by compounding a foaming agent additive with resin or by injecting air or a volatile fluid into the still liquid polymer while it is being processed into a sheet or film. A foamed substrate has an internal structure characterized by a network of gas spaces, or cells, that make such
15 foamed substrate less dense than the solid polymer. The foamed sheets or film substrates used as starting materials in the practice of this invention are flexible, open-celled structures.

- Natural leathers suitable for use in this invention are typically split hides. Synthetic leathers have wide variations in composition (or structure) and properties, but they look like leather in the goods in which they are used. For purposes of technological description, synthetic leathers can be divided into two general categories: coated fabrics
20 and poromerics.

Synthetic leathers which are poromerics are manufactured so as to resemble leather closely in breathability and moisture vapor permeability, as well as in workability, machinability, and other properties. The barrier and permeability properties normally are obtained by manufacturing a controlled microporous (open celled) structure.

- Synthetic leathers which are coated fabrics, like poromerics, have a balance of physical properties and economic
25 considerations. Usually the coating is either vinyl or urethane. Vinyl coatings can be either solid or expanded vinyl which has internal air bubbles which are usually a closed-cell type of foam. Because such structures usually have a non-porous exterior or front surface or face, such structures display poor breathability and moisture vapor transmission. However, since the interior or back surface or face is porous, such a coated fabric can be used in the practice of this invention by applying the polymer to the back face.

5 The fibers utilized in a porous flexible web treated by the methods and apparatus of the present invention can be of natural or synthetic origin. Mixtures of natural fibers and synthetic fibers can also be used. Examples of natural fibers include cotton, wool, silk, jute, linen, and the like. Examples of synthetic fibers include rayon, acetate, polyesters (including polyethyleneterephthalate), polyamides (including nylon), acrylics, olefins, aramids, azlons, glasses, modacrylics, novoloids, nitrils, rayons, sarans, spandex, vinal, vinyon, regenerated cellulose, cellulose acetates, and the like. Blends of natural and synthetic fibers can also be used.

10 With respect to the fluorochemical liquid dispersions (or solutions) which can optionally be used for web pretreatment, the term "impregnation" refers to the penetration of such dispersions into a porous web, and to the distribution of such dispersions in a preferably, substantially uniform and controlled manner in such web, particularly as regards the surface portions of the individual web component structural elements and fibers.

15 With respect to the polymer compositions used in this invention, the term "controlled placement" or "placement" refers to the penetration of such polymer compositions into a porous web, to the distribution of such composition in a controlled manner through such web, and to the resultant, at least partial envelopment of at least a portion of the fibers of such web by such composition in accordance with the present invention, or to the formation of an internal layer, or both.

The word "thixotropy" refers herein to liquid flow behavior in which the viscosity of a liquid is reduced by shear agitation or stirring. It is theorized to be caused by the breakdown of some loosely knit structure in the starting liquid that is built up during a period of rest (storage) and that is torn down during a period of suitable applied stress.

20 The term "coating" as used herein, refers to a generally continuous film or layer formed by a material over or on a surface.

25 The term "internal coating or internal layer" as used herein, refers to a region spaced from the outer surfaces of the web which is substantially continuously filled by the combination of the polymer controllably placed therein and the fibers and filaments of the web in the specified region. Such coating or layer envelopes, and/or surrounds, and/or encapsulates individual fibers, or lines cell or pore walls of the porous web or substrate, in the specified region. The internal layer is not necessarily flat but may undulate or meander through the web, occasionally even touching one or both surfaces of the web.

30 The term "envelop" or "encapsulate" as used interchangeably herein, refers to the partial or complete surrounding, encasement, or enclosing by a discrete layer, film, coating, or the like, of exposed surface portions of at least some individual fiber or lining of a cell or pore wall of a porous web. Such a layer can sometimes be contiguous or integral with other portions of the same enveloping material which becomes deposited on internal areas of a web

which are adjacent to such enveloping layer, enveloped fiber, lined cell or pore wall, or the like.

The term "elastomeric" as used herein refers to the ability of a cured polymer treated web to stretch and return to its original state.

5 The term "curing", or "cure", as used herein, refers to a change in state, condition, and/or structure in a material, such as a curable polymer composition that is usually, but not necessarily, induced by at least one applied variable, such as time, temperature, radiation, presence and quantity in such material of a curing catalyst or curing accelerator, or the like. The term "curing" or "cured" covers partial as well as complete curing. In the occurrence of curing in any case, such as the curing of such a polymer composition that has been selectively placed into a porous flexible substrate or web, the components of such a composition may experience occurrence of one or
10 more of complete or partial (a) polymerization, (b) cross-linking, or (c) other reaction, depending upon the nature of the composition being cured, application variables, and presumably other factors. It is to be understood that the present invention includes polymers that are not cured after application or are only partially cured after application.

15 The term "filled" as used herein in relation to interstices, or interstitial spaces, or open cells, and to the amount of polymer composition therein in a given web, substrate, or the fibers in such web or substrate, designates the presence of such composition therein. When a given interstitial space or open cell is totally taken up by such composition, it is "completely filled" or "plugged". The term "filled" also refers to an interstitial space having a film layer of polymer composition over or through it so that it is closed even though the entire thickness of the interstitial space is not completely filled or plugged.

20 Measurements of the degree of envelopment, interstitial fillage, plugging, or the like in an internal coating are conveniently made by microscopy, or preferably by conventional scanning electron microscopy (SEM) technique. Because of the nature of such measuring by SEM for purposes of the present invention, "a completely filled" interstitial space or open cell can be regarded as a "plugged" interstitial space or open cell.

25 The term "polymeric", or "polymeric" as used herein, refers to monomers and oligomers as well as polymers and polymeric compositions, and mixtures thereof, to the extent that such compositions and mixtures are curable and shear thinnable.

The term "shear thinning", in its broadest sense, means the lowering of the viscosity of a material by the application of energy thereto.

30 A porous web or fabric is preferably untreated or scoured before being treated in accordance with the present invention. Preferably a web can be preliminarily treated, preferably saturated, for example, by padding, to

substantially uniformly impregnate the web with a fluorochemical. Typically, and preferably, the treating composition comprises a dispersion of fluorochemical in a liquid carrier. The liquid carrier is preferably aqueous and can be driven off with heat after application. The treating composition has a low viscosity, typically comparable to the viscosity of water or less. After such a treatment, it is presently preferred that the resulting
5 treated web exhibits a contact angle with water measured on an outer surface of the treated web that is greater than about 90 degrees. The treated web preferably contains fluorochemical substantially uniformly distributed therethrough. Thus, the fluorochemical is believed to be located primarily on and in the individual fibers, cells or pores with the web interstices or open cells being substantially free of fluorochemical.

A presently preferred concentration of fluorochemical in a treatment composition is typically in the range of about
10 1 to about 10% fluorochemical by weight of the total treating composition weight, and more preferably is about 2.5% of an aqueous treating dispersion. Web weight add-ons of the fluorochemical can vary depending upon such factors as the particular web treated, the polymer composition to be utilized in the next step of the treatment process of this invention, the ultimate intended use and properties of the treated web of this invention, and the like. The fluorochemical weight add-on is typically in the range of about 0.01 to about 5% of the weight of the
15 untreated web. After fluorochemical controlled placement, the web is preferably squeezed to remove excess fluorochemical composition after which the web is heated or otherwise dried to evaporate carrier liquid and thereby also accomplish fluorochemical insolubilization or sintering, if permitted or possible with the particular composition used.

The fluorochemical treated web thereafter has a predetermined amount of a curable polymer composition
20 controllably placed within the web by the methods and apparatus of this invention, to form a web whose fibers, cells or pores are at least partially enveloped or lined with the curable polymer composition, whose web outer surfaces are substantially free of the curable polymer, whose web interstices or open cells are not completely filled with the curable polymer and which may also contain an internal layer of polymer. The curable polymer composition utilized preferably exhibits a viscosity greater than 1,000 centipoise and less than 2,000,000
25 centipoise at rest at 25°C at a shear rate of 10 reciprocal seconds.

The fluorochemical residue that remains after web treatment may not be exactly evenly distributed throughout the web, but may be present in the web in certain discontinuities. For example, these discontinuities may be randomly distributed in small areas upon an individual fiber's surface. However, the quantity and distribution of fluorochemical through a web is believed to be largely controllable. Some portions of the fluorochemical may
30 become dislodged from the web and migrate through the polymer due to the forces incurred by the shear thinning and controlled placement of the polymer.

The curable polymer composition is believed to be typically polymeric, (usually a mixture of co-curable polymers and oligomers), and to include a catalyst to promote the cure. The polymers that can be used in the present

invention may be monomers or partially polymerized polymers commonly known as oligomers, or completely polymerized polymers. The polymer may be curable, partially curable or not curable depending upon the desired physical characteristics of the final product. The polymer composition can include conventional additives.

While silicone is a preferred composition, other polymer compositions can include, polyurethanes, fluorosilicones, silicone-modified polyurethanes, acrylics, polytetrafluoroethylene-containing materials, and the like, either alone or in combination with silicones.

It is to be understood that the depth of polymer placement into a web can be controlled by the methods and apparatus herein described to provide selective placement of the polymer within the substrate or web. The web is thereafter optionally cured to convert the curable composition into a solid elastomeric polymer.

The polymer composition is theorized to be caused to flow and distribute itself over fibers, cells or pores in a web under the influence of the processing conditions and apparatus provided by this invention. This flow and distribution is further theorized to be facilitated and promoted by the presence of a fluorochemical which has been preliminarily impregnated into a web, as taught herein. The amount of fluorochemical or fluorochemical residue in a web is believed to influence the amount, and the locations, where the polymer will collect and deposit, and produce encapsulated fibers and/or an internal layer in the web. However, there is no intent to be bound herein by theory.

Some portion of the residue of fluorochemical resulting from a preliminary web saturating operation is theorized to be present upon a treated fiber's surfaces after envelopment of fibers, cells or pores by the polymer has been achieved during the formation of the encapsulating fiber and/or the internal layer by the practice of this invention.

This is believed to be demonstrated by the fact that a web treated by this invention still exhibits an enhanced water and oil repellency, such as is typical of fluorochemicals in porous webs. It is therefore believed that the fluorochemicals are affecting the adherence of the polymer as a thin film enveloping layer about the treated fibers, cells or pores as well as facilitating polymer pressurized flow within and about the interstices or open cells of the web being treated so that the polymer can assume its position enveloping the fibers or lining the cells or pores of the substrate.

In those fabrics that are pretreated with fluorochemicals, the exact interrelationship between the polymer film and the impregnated fluorochemical is presently difficult, or perhaps impossible, to quantify because of the variables involved and because transparent polymer is difficult to observe by optical microscopy. It can be theorized that perhaps the polymer and the fluorochemical each tend to produce discontinuous films upon the fiber surface, and that such films are discontinuous in a complementary manner. It may alternatively be theorized that perhaps the polymer film is contiguous, or substantially so, relative to fluorochemical molecules on a fiber surface, and that the layer of polymer on a fiber surface is so thin that any dislodgement of the fluorochemical may release the

fluorochemical into the polymer film thereby allowing the fluorine to orient or project through the film with the required cure temperature of the polymer, reactivating the water surface contact angle so that the water repellent properties of the fluorochemical affect the finished product. However, regardless of physical or chemical explanation, the combination of polymer film and fluorochemical results in a fiber envelopment or cell or pore wall lining and the formation of encapsulated fibers and/or an internal layer of polymer in a web when this invention is practiced. After curing, the polymer is permanently fixed material.

By using the methods and apparatus of this invention, one can achieve a controlled placement of a polymer composition into a porous substrate or web to obtain a desired treated web.

A curable polymer such as used in the practice of this invention is applied under pressure using shear forces onto and into a web or substrate. The shear forces cause the curable silicone polymer to flow into the web. The extent of fiber envelopment and cell or pore wall lining is believed to be regulatable by controlling such factors as discussed previously, as well as the selection and applied amount of fluorochemical, if any, the curable polymer used, and the applied compressive and shear forces employed at a given temperature so that fiber envelopment is achieved while the interstices and/or open cells of the web are not completely filled with such polymer in the region of the internal layer, and the outer opposed surfaces of the web are substantially completely free of polymer coating or residue. After such a procedure, the curable polymer is then cured.

The curable polymer is applied onto the surface of the web. Then, the web, while tensioned, is passed over and against shearing means or through a compression zone, such as between rollers or against a shear knife. Thus, transversely applied shear force and compressive pressure is applied to the web. The combination of tension, shearing forces, and web speed is sufficient to cause the polymer to move into the web and out from the interstices or open cells around the web fibers, cells, or pores being enveloped. The result is that at least some of the interstices and/or open cells are unfilled in regions of the web outside of the region occupied by the internal coating or internal layer, and are preferably substantially free of polymer. Excess polymer is removed by the surface wiping action of the shearing means. The curable polymer enveloping the fibers is thereafter cured.

The desired penetration of, and distribution and placement of polymer in, a web is believed to be achieved by localized pressuring forces exerted on a web surface which are sufficiently high to cause the viscosity of a polymer composition to be locally reduced, thereby permitting such polymer to flow under such pressuring and to be controllably placed within the web and to envelope its fibers or line the cell or pore walls thereof. To aid in this process, the web is preferably at least slightly distorted by tensioning or stretching, while being somewhat transversely compressed at the location of the controlled placement. This distortion is believed to facilitate the entrance of the polymer composition into the web. When the compression and tension are released, the polymer composition is believed to be squeezed or compressed within and through the interstitial spaces, or open cell spaces, of the treated web.

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If, for example, too much polymer is present in the finished product, then either or both the tension and shear force can be increased, and vice versa for too little polymer. If flow is not adequate upon the fibers, producing incomplete fiber envelopment, then the viscosity of the polymer composition can be reduced by increasing the pressures and temperatures employed for the controlled placement thereof. Alternatively, if the viscosity is too low, then the pressure and/or temperature can be decreased. If the polymer composition is resistant to being positioned or placed in a desired location in a desired amount in a given web at various viscosities and/or pressures, then the level of fluorochemical pretreatment of the web can be increased, or decreased, as the case may be.

In one embodiment of this invention, polymer is forced into a web between two rollers. One such roller bears a polymer impregnant, typically and preferably distributed uniformly upon and over a circumferentially extending textured, or gravure surface. Such roller rotates (i) in the same direction as a facing roller and (ii) oppositely to the direction of movement of a continuously moving web traveling past the localized pressured area achieved between such roller and such moving web. The unidirectional rotation of the two rollers is believed to produce a distorting and stretching force or effect upon the web. This force is believed to promote penetration of the polymer into the web. This form of pressured application or coating can be termed "reverse roll coating" for convenience. Preferably, the reverse coating rollers have generally horizontal axis while the moving web moves generally horizontally. The web is further concurrently both longitudinally tensioned and distorted by being stretched against metering bars, bar knives, and the like which are urged against the web.

Such an initial pressured step is preferably followed by a series of further pressured web treatment steps believed to accomplish polymer reintroduction, polymer distribution, polymer scraping, and excess polymer removal and recovery. The collective result of such steps gradually produces a web wherein the polymer envelopes to a desired extent the fibers, or lines the cell or pore walls comprising the web and collects within a desired internal region or zone in the web thereby filling or plugging interstitial spaces, or open cells or pores, of the web in such region, but not filling the internal structure of the treated web with polymer beyond a desired extent. Particularly, and for example, in a fabric, a polymer composition may be made to substantially completely envelope the fibers or line the cells or pores thereof and fill the interstitial spaces thereof in such internal region.

In another embodiment of this invention, application of polymer to a web occurs from a reservoir. This reservoir of polymer is positioned tightly against the tensioned, moving web (or fabric). The linearly extending, preferably vertically upwardly moving, web (or fabric), constitutes a wall portion of the reservoir. Next, along the path of web travel, a bar or shear knife is pressed strongly and transversely against and laterally across the longitudinally tensioned web (or fabric). Further along the path of web movement, a shear blade or flexible scraper knife is also strongly and transversely forced laterally across and against the tensioned web. More than one shear knife, or more than one flexible compressive knife, can be successively positioned along the path of web movement. These blade means are believed to reintroduce the polymer into the web, to distribute the polymer, and to promote and

complete the envelopment of fibers or lining of the cell or pore walls and fillage of interstices and open cells with polymer, and form an internal coating in a desired region in a web or encapsulate the fibers, or both. These scraper knives or shear blades are also believed to force the polymer further into the three-dimensional structure of the web. Also, these knives, particularly the scraper knives, wipe or scrape excess polymer off the surface of the web, and also extract polymer from within the web, thereby regulating the amount of polymer placed within the web.

The transversely applied shear forces applied across and against the web are sufficiently high to achieve temporarily and locally, a lowering of the viscosity of the preferably thixotropic viscous polymer. The lowered viscosity polymer is thus enabled to flow into, and upon, the internal three-dimensional structure of the web.

Because the polymer composition that is being applied is subject to cure with heat or radiation and time, and because the pressured placement or shear thinning is believed to produce localized heat, the shearing conditions used prior to curing are preferably controlled to minimize premature curing. The properties of the polymer are preferably selected to be such that cure, or excessive cure, does not occur while the web is being treated with polymer during the shear thinning and controlled placement. The cure preferably occurs only after the web controlled placement procedure has been completed. Preferably, the cure temperature of the polymer composition is relatively high (preferably above about 250°F) and the heat exposure time is such as is needed to obtain a desired solid resilient elastomeric polymer.

The viscosity of the polymer is preferably lowered by the high pressure (shear) forces exerted. However, such a pressure- and/or temperature-induced lowered viscosity should not go down too low, otherwise the polymer can flow substantially uncontrolled in the web in the manner of a low viscosity liquid that is saturated and impregnated into a web as in prior art web treatments. If the viscosity of the polymer composition is too low at the time of controlled placement then the web interstices or open cells can become excessively filled therewith, and the polymer is not, for example, reliably and controllably applied to achieve an envelopment of the structural elements (including fibers) of the web being treated together with internal coating formation.

Benzophenones, and particularly 2,4-dihydroxybenzophenone, are believed to be a particularly useful class of additives to the starting polymer composition, as hereinbelow described.

As indicated above, the activity transpiring at a final step in the practice of this invention is generically referred to as curing. Conventional curing conditions known in the prior art for curing polymer compositions are generally suitable for use in the practice of this invention. Thus, temperatures in the range of about 250°F to about 350°F are used and times in the range of about 30 seconds to about 1 minute can be used, although longer and shorter curing times and temperatures may be used, if desired, when thermal curing is practiced. Radiation curing, as with an electron beam or ultraviolet light can also be used. However, using platinum catalysts to accelerate the cure while using lower temperatures and shorter cure times is preferable.

Since either filled, plugged, almost filled interstices, or open cells in the region of an internal layer remain transmissive of air in cured webs made by this invention, the webs are characteristically air permeable or breathable.

Sample webs or fabrics that are beneficially treated, fiber enveloped and internally coated in accordance with the invention include nylon, cotton, rayon and acrylic fabrics, as well as fabrics that are blends of fiber types. Sample nylon fabrics include lime ice, hot coral, raspberry pulp, and diva blue Tactel® (registered trademark of ICI Americas, Inc.) fabrics available from agent Arthur Kahn, Inc. Sample cotton fabrics include Intrepid® cotton cornsilk, sagebrush cotton, and light blue cotton fabrics available also from Arthur Kahn, Inc. Non-woven, monofilamentous, fabrics such as TYVEK® (registered trademark of E.I. duPont de Nemours Co., Inc.) and the like are also employable.

As indicated above, a web is preferably pretreated and impregnated with a fluorochemical prior to being treated with a polymer composition as taught herein. The fluorochemical impregnation is preferably accomplished by first saturating a web with a liquid composition which incorporates the fluorochemical, and then, thereafter, removing the excess liquid composition and residual carrier fluid by draining, compression, drying, or some combination thereof from the treated web.

It is now believed that any fluorochemical known in the art for use in web, particularly fabric treatment in order to achieve water repellency, soil repellency, grease repellency, or the like, can be used for purposes of practicing the present invention. It is believed that a typical fluorochemical of the type used for web treatment can be characterized as a compound having one or more highly fluorinated portions, each portion being a fluoroaliphatic radical or the like, that is (or are) functionally associated with at least one generally non-fluorinated organic portion. Such organic portion can be part of a polymer, part of a reactive monomer, a moiety with a reactable site adapted to react with a binder, or the like. Such a compound is typically applied to a fabric or other web as a suspension or solution in either aqueous or non-aqueous media. Such application may be conventionally carried out in combination with a non-fluorine or fluorine containing resin or binder material for the purpose of providing improved durability as regards such factors as laundering, dry cleaning, and the like.

Fluorochemicals are sometimes known in the art as durable water repellent (DWR) chemicals, although such materials are typically believed to be not particularly durable and to have a tendency to wash out from a fabric treated therewith. In contrast, fiber enveloped webs of this invention which have been pretreated with a fluorochemical display excellent durability and washability characteristics. Indeed, the combination of fluorochemical pretreatment and silicone polymer fiber envelopment such as provided by the present invention appears to provide synergistic property enhancement because the effects or properties obtained appear to be better than can be obtained than by using either the fluorochemical or the silicone polymer alone for web treatment.

Exemplary water repellent fluorochemical compositions include the compositions sold under the name Milease® by ICI Americas Inc. with the type designations F-14N, F-34, F-31X, F-53. Those compositions with the "F" prefix indicate that they contain a fluorochemical as the principal active ingredient. More particularly, Milease® F-14 fluorochemical, for example, is said to contain approximately 18 percent perfluoroacrylate copolymer, 10 percent ethylene glycol (CAS 107-21-1) and 7 percent acetone (CAS 67-64-1) dispersed and dissolved in 65 percent water. Milease® F-31X is said to be a dispersion of a combination of fluorinated resin, acetone, and water.

Still another suitable class of water repellent chemicals is the Phobotex® chemicals of Ciba/Geigy identified as Phototex® FC104, FC461, FC731, FC208 and FC232 which are each believed to be suitable for use, typically in approximately a 5 percent concentration, in saturating a web for use in the invention. These and many other water repellent fluorochemicals are believed to be capable of creating a surface contact angle with water of greater than about 90 degrees when saturated into a web and to be suitable for use in the practice of this invention.

Another group of useful water repellent fluorochemicals is the TEFLON® -based soil and stain repellents of E.I. duPont de Nemours & Co. Inc., 1007 Market Street, Wilmington, DE 19898. Suitable TEFLON® types for use in the practice of this invention include TEFLON® G, NPA, SKF, UP, UPH, PPR, N, and MLV. The active water repellent chemical of each composition is believed to be a fluorochemical in polymeric form that is suitable for dispersion in water, particularly in combination with a cationic surfactant as a dispersant. These dispersions are dilutable in all proportions with water at room temperature. One preferred class of fluorochemical treating compositions useful in the practice of this invention comprises about 1 to about 10 weight percent, more preferably about 5 weight percent of one of the above indicated TEFLON®-type water repellent fluorochemicals in water.

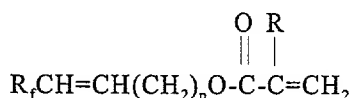
Another major group of suitable water repellent fluorochemical compositions useful in the practice of the invention is commercially available under the designation ZEPEL® rain and stain repellent chemicals of E.I. duPont de Nemours & Co. Inc., such as ZEPEL® water repellent chemicals types B, D, K, RN, RC, OR, HT, 6700 and 7040. Each is believed to be a fluorochemical in polymeric form that is dispersible in all proportions at room temperature. The dispersants ZEPEL® B, D, K, and RN are believed to be cationic, while the dispersant ZEPEL® RC is believed to be nonionic.

As an exemplary composition, ZEPEL® 6700 is said to be comprised of 15 to 20 percent perfluoroalkyl acrylic copolymer, 1 to 2 percent alkoxyated carboxylic acid, and 3 to 5 percent ethylene glycol. Exemplary characteristics of the composition include a boiling point of 100°C at 760 mm Hg and a specific gravity of 1.08. The volatiles are approximately 80 percent by weight. The pH is 2 to 5. The odor is mild; the concentrate form is that of a semi-opaque liquid; and the concentrate color is straw white. The composition and characteristics of ZEPEL® 7040 repellent chemical are believed to be substantially identical to those of ZEPEL® 6700 except that

the former composition additionally contains 7 to 8 percent acetone.

Another major group of water repellent fluorochemicals comprises the Scotchgard® water repellent chemicals of 3M Co., St. Paul, Minnesota. The Scotchgard® fluorochemicals are believed to be aqueously dispersed fluorochemicals in polymeric form. The compositions of two suitable Scotchgard® water repellent fluorochemicals are believed to be disclosed in U.S. Patent Nos. 3,393,186 and 3,356,628, which patents are incorporated herein by reference. Thus, the Scotchgard® fluorochemical of U.S. Patent No. 3,356,628 consists of copolymers of perfluoroacrylates and hydroxyalkyl acrylates. These copolymers are suitable for use as an oil and water repellent coating on a fibrous or porous surface. They have a carbon to carbon main chain and contain recurring monovalent perfluorocarbon groups having from 4 to 18 carbon atoms each and also having recurring hydroxyl radicals. From 20 to 70 percent of the weight of such copolymer is contributed by fluorine atoms in the perfluorocarbon groups and from 0.05 to 2 percent of the weight of the copolymer is contributed by the hydroxyl radicals. Such copolymer is said to have improved surface adherability properties as compared to the homopolymer of a corresponding fluorocarbon monomer.

The Scotchgard® fluorochemical of U.S. Patent No. 3,393,186 consists of perfluoroalkenylacrylates and polymers thereof. An exemplary fluorinated monomer has the formula:



Wherein R_f is a fluorocarbon group having from 3 to 18 carbon atoms, R is hydrogen or methyl, and n is 0-16. Such a water repellent fluorochemical composition is supplied and saturated into the substrate web as a readily pourable aqueous dispersion.

U.S. Patent No. 4,426,476 discloses a fluorochemical textile treating composition containing a water-insoluble fluoroaliphatic radical, an aliphatic chlorine-containing ester and a water insoluble, fluoroaliphatic radical containing polymer.

U.S. Patent No. 3,896,251 discloses a fluorochemical textile treating composition containing a fluoroaliphatic radical containing linear vinyl polymer having 10 to 60 weight percent fluorine and a solvent soluble carbodiimide preferably comprising fluoroaliphatic groups. A table in this patent lists a plurality of prior art fluoroaliphatic

radical containing polymers useful for the treatment of fabrics and the prior art patents where such polymers are taught.

U.S. Patent No. 3,328,661 discloses textile treating solutions of a copolymer of an ethylenically unsaturated fluorocarbon monomer and a ethylenically unsaturated epoxy group containing monomer.

- 5 U.S. Patent No. 3,398,182 discloses fluorocarbon compounds useful for fabric treatment that contain a highly fluorinated oleophobic and hydrophobic terminal portion and a different nonfluorinated oleophilic portion linked together by a urethane radical.

Water repellent fluorochemical compositions are preferably utilized to saturate a starting untreated porous web substrate so that such composition and its constituents wet substantially completely and substantially uniformly
10 all portions of the web. Such a saturation can be accomplished by various well known techniques, such as dipping the web into a bath of the composition, or padding the composition onto and into the web, or the like. Padding is the presently preferred method of fluorochemical application.

After application of the fluorochemical composition to the web, the water (or liquid warier) and other volatile components of the composition are removed by conventional techniques to provide a treated web that contains
15 the impregnated fluorochemical throughout the web substrate.

In a preferred procedure of fluorochemical controlled placement, a web is substantially completely saturated with an aqueous dispersion of a fluorochemical. Thereafter, the resulting impregnated web is compressed to remove excess portions of said dispersion. Finally, the web is heated to evaporate the carrier liquid. If the fluorochemical is curable, then the heating also accomplishes curing. After the fluorochemical treatment, the fluorochemical is
20 found only on or in the web structural elements or fibers and is substantially completely absent from the web interstices.

The fluorochemical concentration in the treating composition is such as to permit a treated fluorochemical containing web, after volatiles of the treating composition are removed, to exhibit a contact angle with water applied to an outer web surface which is greater than about 90°. More preferably, the contact angle provided is
25 greater than about 130°.

The web weight add-on provided by the fluorochemical after removal of volatiles is usually relatively minor. However, the weight add on can vary with such factors as the nature of web treated, the type of polymer composition utilized in the next step of the process, the temperature at which the composition is applied, the ultimate use contemplated for a web, and the like.

Typical weight add-ons of fluorochemical are in the range of about 1 to about 10 percent of the original weight of the web. More preferably, such weight add-ons are about 2 to about 4 weight percent of the weight of the starting fabric.

5 Durability of a web that has been treated with a fluorochemical and durability of a web that is subsequently treated with a polymer can sometimes be improved by the conventional process of "sintering". The exact physical and chemical processes that occur during sintering are unknown. The so-called sintering temperature utilized is a function of the fluorochemical composition utilized and such temperature is frequently recommended by fluorochemical manufacturers. Typically, sintering is carried out at a temperature of about 130 to about 160°C for a period of time of about 2 to about 5 minutes. Acid catalysts can be added to give improved durability to
10 laundering and dry cleaning solvents.

The fluorochemical is believed to provide more than water or other repellent properties to the resulting treated web, particularly since the curable polymer is often itself a water repellent. Rather, and without wishing to be bound by theory, it is believed that the fluorochemical in a treated web provides relative lubricity for the treated fibers during the pressure application of the curable polymer. The polymer is applied under pressures which can
15 be relatively high, and the polymer is itself relatively viscous, as is discussed herein. In order for the curable polymer to coat and envelop web fibers, but not fill web interstitial voids, the fibers of the web may move over and against each other to a limited extent, thereby to permit entry of the polymer into and around the fibers. It is thought that the fluorochemical deposits may facilitate such fiber motion and facilitate envelopment during the pressure application and subsequent shearing processing.

20 Alternatively, the fluorochemical may inhibit deposition of the polymer at the positions of the fluorochemical deposits which somehow ultimately tends to cause thin enveloping layers of polymer to form on fibers.

The precise physics and chemistry of the interaction between the fluorochemical and the polymer is not understood. A simple experiment demonstrates movement of the liquid polymer as influenced by the presence of the fluorochemical:

25 A piece of fabric, for example the Red Kap Milliken poplin polyester cotton blend fabric, is cut into swatches. One swatch is treated with an adjuvant, for example a three percent solution of the durable water-repellent chemical Milease® F-31X. The treated swatch and an untreated swatch are each positioned at a 45° angle to plumb. A measured amount, for example one-half ounce, of a viscous polymer composition, for example the Mobay® 2530A/B silicon composition, is dropped onto the inclined surface of each swatch. The distance in
30 centimeters that the composition flows downwards upon the surface of the swatch is measured over time, typically for 30 minutes.

A graphical plot of the flow of the silicone composition respectively upon the untreated and treated swatches over time can be prepared, such as shown in Figure 1. At the expiration of 30 minutes the viscous composition has typically traveled a distance of about 8.8 centimeters upon the treated swatch, or a rate of about 0.29 centimeters per minute. At the expiration of the same 30 minutes, the viscous composition has typically traveled a lesser distance of about 7.1 centimeters upon the untreated swatch, or a rate of about 0.24 centimeters per minute. Qualitatively commensurate results are obtainable with other DWR fluorochemical adjuvants that facilitate the viscous flow of polymer compositions in accordance with the invention. Indeed, if desired, the simple flow rate test can be used to qualify an adjuvant compound for its employment within the method of the invention. The fluorochemical pretreated web generally increases the surface contact angle of the polymer while reducing the amount of saturation of the polymer into the fibers themselves.

The fluorochemical treated web is thereafter treated under pressure with a predetermined amount of a curable polymer composition to form a web whose fibers are preferably substantially completely enveloped with such curable polymer and whose outer surfaces and interstices are preferably substantially completely free of the curable polymer. The polymer is thereafter cured by heat, radiation, or the like. Even room temperature curing can be used. A polymer impregnated, fluorochemical pretreated web can be interveningly stored before being subjected to curing conditions depending upon the storage or shelf life of the treating silicone polymer composition.

A curable polymer composition utilized in the practice of this invention preferably has a viscosity that is sufficient to achieve an internal coating of the web. Generally, the viscosity is greater than about 1000 centipoise and less than about 2,000,000 centipoise at a shear rate of 10 reciprocal seconds. It is presently most preferred that such composition have a viscosity in the range of about 5,000 to about 1,000,000 centipoise at 25°C. Such a composition is believed to contain less than about 1% by weight of volatile material.

The polymer is believed to be typically polymeric and to be commonly a mixture of co-curable polymers, oligomers, and/or monomers. A catalyst is usually also present, and, for the presently preferred silicone polymer compositions discussed hereinafter, is platinum or a platinum compound, such as a platinum salt.

A preferred class of liquid curable silicone polymer compositions comprises a curable mixture of the following components:

- (A) at least one organo-hydrosilane polymer (including copolymers);
- (B) at least one vinyl substituted polysiloxane (including copolymers);
- (C) a platinum or platinum containing catalyst; and
- (D) (optionally) fillers and additives.

Typical silicone hydrides (component A) are polymethylhydrosiloxanes which are dimethyl siloxane copolymers. Typical vinyl terminated siloxanes are vinyl dimethyl terminated or vinyl substituted polydimethylsiloxanes. Typical catalyst systems include solutions or complexes of chloroplatinic acid in alcohols, ethers, divinylsiloxanes, and cyclic vinyl siloxanes.

- 5 The polymethylhydrosiloxanes (component A) are used in the form of their dimethyl copolymers because their reactivity is more controllable than that of the homopolymers and because they result in tougher polymers with a lower cross-link density. Although the reaction with vinyl functional silicones (component B) does reportedly take place in 1:1 stoichiometry, the minimum ratio of hydride (component A) to vinyl (component B) in commercial products is reportedly about 2:1 and may be as high as 6:1. While the hydrosilation reaction of polymethylhydrosilane is used in both so called RTV (room temperature vulcanizable) and LTV (low temperature vulcanizable) systems, and while both such systems are believed to be useful in the practice of the present invention, systems which undergo curing at elevated temperature are presently preferred.

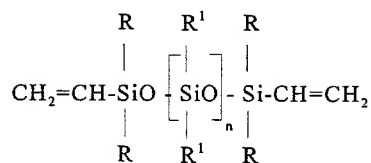
Elastomers produced from such a curing reaction are known to demonstrate toughness, tensile strength, and dimensional stability.

- 15 Particulate fillers are known to be useful additives for incorporation into liquid silicone polymer compositions. Such fillers apparently not only can extend and reinforce the cured compositions produced therefrom, but also can favorably influence thixotropic behavior in such compositions. Thixotropic behavior is presently preferred in compositions used in the practice of this invention. A terminal silanol (Si-OH) group makes such silanol siloxanes susceptible to reaction in curing, as is believed desirable.
- 20 It is believed that all or a part of component B can be replaced with a so called silanol vinyl terminated polysiloxane while using an organotin compound as a suitable curing catalyst as is disclosed in U.S. Patent No. 4,162,356. However, it is presently preferred to use vinyl substituted polysiloxanes in component B.

- A polymer composition useful in this invention can contain curable silicone resin, curable polyurethane, curable fluorosilicone, curable modified polyurethane silicones, curable modified silicone polyurethanes, curable acrylics, polytetrafluoroethylene, and the like, either alone or in combination with one or more compositions.

One particular type of silicone composition which is believed to be well suited for use in the controlled placement step of the method of the invention is taught in U.S. Patent Nos. 4,472,470 and 4,500,584 and in U.S. Patent No. 4,666,765. The contents of these patents are incorporated herein by reference. Such a composition comprises in combination:

- 30 (i) a liquid vinyl chain-terminated polysiloxane having the formula:



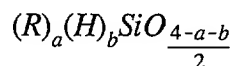
wherein R and R¹ are monovalent hydrocarbon radicals free of aliphatic unsaturation with at least 50 mole percent of the R¹ groups being methyl, and where n has a value sufficient to provide a viscosity of about 500 centipoise to about 2,000,000 centipoise at 25°C;

(ii) a resinous organopolysiloxane copolymer comprising:

- (a) (R²)₃SiO_{0.5} units and SiO₂ units, or
- (b) (R³)₂SiO_{0.5} units, (R³)₂SiO units and SiO₂ units, or
- (c) mixtures thereof, where R² and R³ are selected from the group consisting of vinyl radicals and monovalent hydrocarbon radicals free of aliphatic unsaturation, where from about 1.5 to about 10 mole percent of the silicon atoms contain silicon-bonded vinyl groups, where the ratio of monofunctional units to tetrafunctional units is from about 0.5:1 to about 1:1, and the ratios of difunctional units to tetrafunctional units ranges up to about 0.1:1;]

(iii) a platinum or platinum containing catalyst; and

(iv) a liquid organohydrogenpolysiloxane having the formula:



- 15 in an amount sufficient to provide from about 0.5 to about 1.0 silicon-bonded hydrogen atoms per silicon-bonded vinyl group of above component (i) or above subcomponent (iii) of, R_k is a monovalent hydrocarbon radical free of aliphatic unsaturation, and has a value of from about 1.0 to about 2.1, b has a value of from about 0.1 to about 1.0, and the sum of a and b is from about 2.0 to about 2.7, there being at least two silicon-bonded hydrogen atoms per molecule.

Optionally, such a composition can contain a finely divided inorganic filler (identified herein for convenience as component (v)).

For example, such a composition can comprise on a parts by weight basis:

- (a) 100 parts of above component (i);
- (b) 100-200 parts of above component (ii);
- (c) a catalytically effective amount of above component (iii), which, for present illustration purposes, can range from about 0.01 to about 3 parts of component (iii), although larger and smaller amounts can be employed without departing from operability (composition curability) as those skilled in the art will appreciate;
- (d) 50-100 parts of above component (iv), although larger and smaller amounts can be employed without departing from operability (curability) as those skilled in the art will appreciate; and
- (e) 0-50 parts of above component (v).

Embodiments of such starting composition are believed to be available commercially from various manufacturers under various trademarks and trade names.

As commercially available, such a composition is commonly in the two-package form (which are combined before use). Typically, the component (iv) above is maintained apart from the components (i) and (ii) to prevent possible gelation in storage before use, as those skilled in the art appreciate. For example, one package can comprise components (i) and (ii) which can be formulated together with at least some of component (ii) being dissolved in the component (i), along with component (iii) and some or all of component (v) (if employed), while the second package can comprise component (iv) and optionally a portion of component (v) (if employed). By adjusting the amount of component (i) and filler component (v) (if used) in the second package, the quantity of catalyst component (iii) required to produce a desired curable composition is achieved. Preferably, component (iii) and the component (iv) are not included together in the same package. As is taught, for example, in U.S. Patent No. 3,436,366 (which is incorporated herein by reference), the distribution of the components between the two packages is preferably such that from about 0.1 to 1 part by weight of the second package is employed per part of the first package. For use, the two packages are merely mixed together in suitable fashion at the point of use. Other suitable silicone polymer compositions are disclosed in the following U.S. patents:

U.S. Patent No. 4,032,502 provide compositions containing a linear polydiorganosiloxane having two siloxane bonded vinyl groups per molecule, organosiloxane that is soluble in such linear polydiorganosiloxane and comprised of a mixture of a polyorganosiloxane and a polydiorganosiloxane, platinum-containing catalyst, a platinum catalyst inhibitor, and a reinforcing silica filler whose surface

has been treated with an organosilicone compound.

U.S. Patent No. 4,108,825 discloses a composition comprising a triorganosiloxy end-blocked polydiorganosiloxane, an organohydrogensiloxane having an average of at least 2.1 silicon-bonded hydrogen atoms per molecule, a reinforcing silica filler having a surface treated with an organosilicone compound, a platinum catalyst, and ceric hydrate. Such silicone polymer composition is desirable when a web is being prepared which has flame retardant properties.

U.S. Patent No. 4,162,243 discloses a silicone composition of 100 parts by weight triorganosiloxy end-blocked polydimethylsiloxane, reinforcing amorphous silica that is surface treated with organosiloxane groups, organohydrogensiloxane, and platinum catalyst.

U.S. Patent No. 4,250,075 discloses a liquid silicone polymer composition that comprises vinyl diorganosiloxy end-blocked polydiorganosiloxane, polyorganohydrogensiloxane, platinum catalyst, platinum catalyst inhibitor, and carbonaceous particles. Such a silicone polymer composition is useful when a web of this invention is being prepared that has electrically conductive properties.

U.S. Patent No. 4,427,801 discloses a curable organopolysiloxane of liquid triorganosiloxy end-blocked polydiorganosiloxane wherein the triorganosiloxy groups are vinyl dimethylsiloxy or vinylmethylphenylsiloxy, finely divided amorphous silica particles treated with mixed trimethylsiloxy groups and vinyl-containing siloxy groups, organopolysiloxane resin containing vinyl groups, organohydrogensiloxane, and a platinum containing catalyst.

U.S. Patent No. 4,500,659 discloses a silicone composition of liquid triorganosiloxy end-blocked polydimethylsiloxane wherein the triorganosiloxy units are dimethylvinylsiloxy or methylphenylvinylsiloxy, a reinforcing filler whose surface has been treated with a liquid hydroxyl end-blocked polyorganosiloxane which is fluorine-substituted, a liquid methylhydrogensiloxane, and a platinum-containing catalyst.

U.S. Patent No. 4,585,830 discloses an organosiloxane composition of a triorganosiloxy end-blocked polydiorganosiloxane containing at least two vinyl radicals per molecule, an organohydrogensiloxane containing at least two silicon-bonded hydrogen atoms per molecule, a platinum-containing hydrosilation catalyst, optionally a catalyst inhibitor, a finely divided silica filler, and a silica treating agent which is at least partially immiscible with said polydiorganosiloxane.

U.S. Patent No. 4,753,978 discloses an organosiloxane composition of a first diorganovinylsiloxy terminated polydiorganosiloxane exhibiting a specified viscosity and having no ethylenically unsaturated

hydrocarbon radicals bonded to non-terminal silicon atoms, a second diorganovinylsiloxyl terminated polydiorganosiloxane that is miscible with the first polydiorganosiloxane and contains a vinyl radical, an organohydrogensiloxane, a platinum hydrosilation catalyst, and a treated reinforcing silica filler.

5 U.S. Patent No. 4,785,047 discloses silicone elastomers having a mixture of a liquid polydiorganosiloxane containing at least two vinyl or other ethylenically unsaturated radicals per molecule and a finely divided silica filler treated with a hexaorganodisilazane which mixture is then compounded with additional hexaorganodisiloxane.

10 U.S. Patent No. 4,329,274 discloses viscous liquid silicone polymer compositions that are believed to be suitable and which are comprised of vinyl containing diorganopolysiloxane (corresponding to component B), silicon hydride siloxane (corresponding to component A) and an effective amount of a catalyst which is a halogenated tetrameric platinum complex.

U.S. Patent No. 4,442,060 discloses a mixture of 100 parts by weight of a viscous diorganopolysiloxane oil, 10 to 75 parts by weight of finely divided reinforcing silica, 1 to 20 parts by weight of a structuring inhibitor, and 0.1 to 4 parts by weight of 2,4-dichlorobenzoyl peroxide controlled cross-linking agent.

15 Silicone resin compositions shown in the table below have all been used in the practice of this invention. Such compositions of Table I are believed to involve formulations that are of the type hereinabove characterized.

Table I
Illustrative Starting Polymer Compositions

MANUFACTURER	TRADE DESIGNATION	COMPONENTS ⁽¹⁾
20 Mobay	Silopren® LSR 2530	Vinyl-terminated polydimethylsiloxane with fumed silica, methylhydrogen polysiloxane
Mobay	Silopren® LSR 2540/01	
Dow Corning	Silastic® 595 LSR	Polysiloxane
General Electric	SLE 5106	Polysiloxane
General Electric	SLE 5106	Siloxane resin solution
25 General Electric	SLE 5300	Polysiloxane
General Electric	SLE 5500	Polysiloxane
Shin-Etsu	KE 1917	
Shin-Etsu	DI 1940-30	
30 SWS Silicones Corporation	Liquid Rubber BC-10	Silicone fluid with silicone dioxide filler and curing agents

GE SLE 5110		Polysiloxane
GE SLE 6108		Polysiloxane

Table I footnote:

(1) Identified components do not represent complete composition of the individual products shown.

- 5 When a polymer composition of a silicone polymer and a benzophenone is pressured into a porous web as taught herein, protection of an organic web against ultraviolet radiation is improved, and the degradation effects associated with ultraviolet light exposure are inhibited, as may be expected from prior art teachings concerning the behavior of benzophenones.

- Surprisingly and unexpectedly, however, when silicone polymer compositions such as used in this invention
10 contain a benzophenone, the resulting composition is believed to display improved viscosity characteristics, particularly thixotropic characteristics, and also curing acceleration, when such a composition is subjected to high shear forces.

A presently preferred benzophenone additive useful in the present invention is 2,4-dihydroxybenzophenone.

- The regulation of internal and external rheology, and of viscosity, achieved in a characteristically highly viscous
15 polymer composition of the invention is believed to be an important and desirable feature of the benzophenone and silicone polymer compositions which find use in internally coated web manufacture as taught herein.

- In such compositions useful in the present invention, a control of compositional rheology, and particularly of complex viscosity, is accomplishable, if desired, by the selective addition of diluent and additives. These polymer compositions characteristically exhibit performance curves indicating substantially level and constant loss
20 modulus, storage modulus, and complex viscosity over extended temperature ranges. The graphic plots of loss modulus, storage modulus, and complex viscosity versus temperature all are believed to characteristically exhibit a sharp knee that shows the moduli to increase in value rapidly at cure temperatures.

- Preferably, the curing proceeds to a point where the polymer composition is no longer sticky, or tacky, but preferably curing is not allowed to continue to a point where the resulting polymer composition becomes
25 excessively hard, rigid, or brittle. Compositions of this invention are controllably curable into polymeric materials which are preferably not sticky or tacky, and which have desirable elastomeric, flexural, and resiliency characteristics.

- The contact angle exhibited by a silicone composition used in this invention varies with the particular web which is to be saturated therewith. However, the contact angle of water is generally lower for the non-treated side than
30 the treated side. A combination of the processed web, the silicone polymer and the fluorochemical generally

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produces higher water contact angles than webs treated only with fluorochemicals. The performance of a polymer composition may be determined by the nature of a previously applied saturant such as a fluorochemical. Suitable starting compositions include 100% liquid curable silicone rubber compositions, such as SLE5600 A/B from General Electric, Mobay LSR 2580A/B, Dow Corning Silastic® 595 LSR and Silastic® 590 which when
5 formulated with substituted benzophenone as taught herein will form a contact angle of much greater than 70 degrees, and typically of 90+ degrees, with typical porous webs (such as fabrics) that have a residue of fluorochemical upon (and within) the web from a prior saturation.

10 The polymer composition used in the practice of this invention can also carry additives into the three-dimensional structure of the web during the pressured application. Further, it is preferable, that any additives be bound into the cured composition permanently as located in the three-dimensional structure of the web. Particularly in the case of fabrics, this desirably positions the additives mainly on surface portions of the encapsulated yarns and fibers in positions where they typically are beneficially located and maintained, or on the surfaces of the internal layer, or on the surfaces of the web, or some combination thereof.

15 Control of the pressurized application step can be provided at a number of areas since the shear process is sensitive to the viscosity of the polymer composition both at atmospheric pressure and at superatmospheric pressure. The ambient temperature affecting the polymer as it is applied, and the pressure-induced temperature changes occurring during controlled placement of the polymer also play roles in viscosity and therefore the shear process. Of course, the chemical composition of the polymer composition also plays a role in the shear process and assists in the formation of an internal layer and/or internal encapsulation of the fibers or structural elements
20 of the web.

The amount of polymer utilized and the weight add-on thereof are again variable and dependent upon several things such as the treated web, the desired end use of the web, cost and the like. Web weight add-ons can be as little as about 5 weight percent up to about 200 weight percent of the untreated web. For producing breathable, water-repellent fabric webs of this invention, weight add-ons are preferably in the range of about 10 to about 100
25 weight percent of the weight of the untreated web.

30 The fluorochemical saturant composition may also contain a bonding agent. The bonding agent can facilitate the bonding of the water repellent chemical and/or the impregnate to the three-dimensional structure of the web within which it is saturated. Mobay Silopren™ bonding agent type LSR Z 3042 and Norsil 815 primer are representative compositions that can be used to facilitate bonding of the water repellent chemicals and/or impregnant to and within the web. Use of the bonding agents is not essential to the practice of this invention, but may improve bonding of the fluorochemical and/or the polymer composition to fibers.

The fluorochemical particularly, and also the bonding agents when used, are preferably affixed to the

three-dimensional structure of the web prior to the controlled placement of polymer within the web. Complete affixing is not necessary for the fluorochemical. The fluorochemical will apparently facilitate the pressured application of a polymer composition even if the fluorochemical is not preliminarily fixed within or located within the web being treated. However, fixing, especially by sintering, appears to cause the water repellent chemicals to flow and to become better attached to the three-dimensional structure of the web. In this regard, a lesser amount of fluorochemical will remain in place better, and will better facilitate the subsequent pressured application of the polymer, if the sintering or insolubilizing step is performed prior to such a pressured application.

After fluorochemical saturation followed by controlled polymer placement and curing, a web may have a surface contact angle with the polymer of greater than about 70 degrees, and more typically greater than about 90 degrees. Web pressures can involve transverse force or pressure in the range of tens to thousands of pounds per square inch of web surface.

Similar to the functional qualifications achieved by the use of a fluorochemical in the preferred saturating pretreatment step, the polymer introduced by the pressured application step can be defined by its functional qualifications. For example, the silicone polymer produces a contact angle with a fluorochemical treated web of greater than about 70 degrees. The contact angle of a web with a fluorochemical will be within a range of about 90 degrees to about 180 degrees while the contact angle of a fluorochemically treated web with the silicone polymer will be within a range of about 70 degrees to about 180 degrees.

The contact angle exhibited by the silicone polymer can be, if desired, qualified against the particular web saturated with the particular fluorochemical saturant. The selection of a suitable silicone polymer composition may be determined by the nature of the previously applied fluorochemical saturant. The fluorochemical saturant and silicone polymer compositions are, however, not critical to the practice of this invention since wide respective compositional ranges may be involved. In particular, a substantially undiluted liquid silicon rubber which is available from suppliers, such as GE, Dow Corning, and Mobay-Bayer, will characteristically form a contact angle of much greater than about 70 degrees, and typically greater than about 90 degrees, with typical porous webs (such as fabrics) that have a residue of fluorochemical upon (and within) the web resulting from a prior saturation.

The polymer composition can carry additives into the three-dimensional structure of the web in the pressured application steps of the method of the invention. Further, the polymer composition, when cured, is capable of adhering to structural elements, fibers, yarns, and the like, and any additives dispersed therein. Thus, additives are positioned adjacent to or on surfaces of structural elements, yarns, fibers and the like, in a position where they can be beneficial.

Examples of additives that are dispersible in effective amounts in a viscous polymer composition typically at a concentration of about 0.1 to 20 weight percent (based on total composition weight) include ultraviolet absorbers, flame retardants, aluminum hydroxide, filling agents, blood repellents, flattening agents, optical reflective agents, hand altering agents, biocompatible proteins, hydrolyzed silk, and the like. Hydrolyzed silk is a texturing agent that imparts a substantially silky feel to a fabric treated in accordance with the method of the invention regardless of whether or not such treated web or fabric is itself silk.

Examples of other polymer dispersible agents include those affecting thermal conductivity, radiation reflectivity, electrical conductivity, and other properties. For example, if a metallic sheen and/or thermal or electrical conductivity or infrared background blending is desired, powdered metals may be dispersed therein.

10 The pressured application of the polymer is sensitive to the viscosity of the polymer composition. Temperature affects the polymer composition by reducing or altering its viscosity. Shear-induced temperature changes occurring during application or during subsequent shear processing of the polymer can affect viscosity. The chemical composition of the polymer also plays a role in the treating process and effects in the treatment of web structural elements (including fibers) and the regulation of the filling of interstices and open cell voids.

15 Various machines and procedures can be used for performing the process of the invention. Illustrative machines and processes of use which are suitable for use in the practice of this invention, are now described.

An embodiment of apparatus in accordance with this invention is illustrated in the side elevational view in Figure 4a. Two blades 200 and 210 in opposed relationship to one another are provided in functional combination with means for providing a precisely adjustable gap therebetween through which a web or fabric 300 is drawn while having a polymer composition 220 applied to either one or both surfaces thereof. An enlarged side view of a typical blade 200 or 210 is shown in Figure 4b. Dimensions A, B, C, D, and E are typically and exemplarily illustrated as, respectively, about 3-1/2 inches, about 1-1/2 inches, about 2 inches, about 1/2 inch, and about 5/16 inch. The narrow edge is preferably milled to a tolerance of about 1/10,000 inch continuously along the edge surface of each blade which is typically and illustratively about 38 inches long. Each of the corners of the narrow edge is preferably and illustratively a hard (not beveled or ground) angular edge. Each blade 200 or 210 is typically and illustratively made from carbon steel or stainless steel. The entry angle of the web 300 with the blade is generally not altered in the apparatus of Figure 4a. Therefore, for purposes of the apparatus illustrated in Figure 4a, the blade shown in Figure 4b has a leading edge 260 and a trailing edge 250.

A reservoir of polymer composition is formed preferably on one upper surface of the web or fabric 300 behind (relative to the direction of web movement) an upper one of the blades 200 and 210 which are mounted on a frame (not shown) so as to extend horizontally. As the fabric 300 is drawn through the slit orifice defined between blades 200 and 210, some polymer becomes entrained on the web or fabric surface and moves through such slit

orifice, thereby accomplishing pressurized application of the polymer into the web or fabric 300. The slit orifice gap is chosen preferably and illustratively to be slightly smaller than the relaxed thickness of the starting web or fabric.

Referring to Figure 4a, a second pressured application station is seen to be positioned downstream (relative to the direction of fabric movement) from the pair of opposed blades 200 and 210. While the blades are shown positioned directly opposed to one another, they may be offset so that the advancing web first contacts one blade and then the other. In such a configuration, the blades may also be adjusted to some angle other than 90° to the web, and blade adjustment facilities (not shown) can be used to accomplish this. At this station, a knife blade 230 is provided which has an edge that presses against the web or fabric 300 to reintroduce the polymer composition into the fabric 300. One side of blade 230, adjacent to the edge thereof, is strongly biased against an adjacent cylinder or bar 240, which, in the embodiment shown, does not rotate. If desired, bar 240 can be journaled for rotational movement. As the fabric is moved between the blade 230 and the bar 240, it is preferably uniformly compressed. Preferably, the compression force is in the range of about 10 to about 500 pounds per linear inch, although higher and lower forces can be employed. As the fabric 300 passes over the edge of blade 230, it is drawn away at an angle from the blade edge under longitudinal tension. For example, longitudinal tension in the range of from about 0.5 to 10 pounds per inch can be employed. Such pressured application or controlled placement serves to distribute and reintroduce the polymer composition in the web. Excess polymer composition is removed by blade scraping. Passage of the fabric 300 between the blade 230 and the bar 240 and over the edge of the blade 230 is believed to produce shear forces in the polymer composition 220 (within the fabric 300) that facilitate flow and distribution thereof within the three-dimensional matrix of the fabric 300. Concurrently, blade 230 also scrapes excess polymer composition off the fabric's surface in contact with the edge of blade 230.

Both the steps of fluorochemical saturation and of subsequent polymer composition controlled placement are performable, if desired, in production volumes, and at speeds which can be typical of the so-called high end range of fabric finishing lines. The fluorochemical saturation is conveniently accomplished conventionally by using a padbath in which the fabric is run through a dilute treating bath followed by squeeze rollers to remove excess liquid and overdrying. In general, any method of applying the fluorochemical would be acceptable. Typically, the web is treated with a fluorochemical and wound on a roll before it is introduced into apparatus of this invention apparatus although, if desired, the fluorochemical treatment could be in-line.

Another embodiment of a machine suitable for accomplishing controlled placement of polymer within a web in accordance with this invention is shown diagrammatically in Figure 5. At a treatment or control head, pressurized introduction of the polymer composition into the web is first carried out. At a subsequent stage, controlled pressure reintroduction, distribution, and metering of the polymer composition and recovery of excess polymer transpires using a shear knife or blade which applies transverse force against the treated web laterally across the web. In a subsequent stage, further controlled pressure reintroduction and metering takes place by

means of another blade, either flexible or rigid, such as, for example, a so-called flex-knife or Spanish knife. Here, additional recovery of excess liquid polymer is accomplished. In all knife-applying states, the excess polymer removed is collected and preferably passed by a recycling system back to the initial, pressured introduction stage to achieve process operating economies. Still further successive polymer pressure reintroduction stages may be used if desired. The direction of the arrows in the diagrammatic representation of Figure 5 shows the general direction of movements in the region of the treatment head, including the general direction of polymer movement in the practice of such process.

The apparatus employed in the present invention functions first to apply and preferably concurrently to shear thin and place a polymer composition into a web under pressure. Such polymer composition is then reintroduced, distributed, and metered in a controlled manner in the web with the aid of transversely applied shearing force and compressive force such that the polymer composition becomes distributed in the web so that an internal layer of polymer is formed while the fibers are at least partially enveloped while the interstices or open cells are substantially completely filled with the polymer composition in the region of the internal coating, and/or the fibers within the web are partially or fully encapsulated. During treatment, the web is longitudinally tensioned and the pressurized application and the subsequent shearing and compressive actions are successively accomplished in localized zones preferably extending generally laterally across the web (that is, generally perpendicularly to the direction of such longitudinal web tensioning) using transversely applied force exerted locally against surface portions of the web during each controlled placement and shearing operation. The web is conveniently and preferably, but not necessarily, moved longitudinally relative to such laterally extending web processing zones. In treating short lengths of a fabric, the blades may be moved relative to a stationary length of fabric. The pressurized application, shearing and compressing steps are preferably carried out successively or sequentially. Such zones are themselves preferably at stationary locations while the web is moved, but if desired, the web can be stationary while the zones are moved, or both. The result is that the polymer composition flows into the web and is distributed internally generally uniformly to a predeterminable and controllable extent.

A schematic side elevational view of another embodiment of a suitable machine for use in the practice of the invention is shown in Figure 6. This machine continuously moves a longitudinally tensioned web 60 successively through a pressure station which incorporates a reverse roll coater having rollers 10 and 11, a shear station which incorporates a shear knife 20, and a finishing station which employs at least one so called flex-knife (or Spanish knife) 30. A typical shear knife is illustratively shown in Figure 4b. for purposes of the apparatus shown in Figure 6, the knife shown in Figure 4b has a leading edge 250 and a trailing edge 260. Optionally, but preferably (for reasons of process operating economics) excess polymer composition that is removed from web surfaces in the shear station and finishing station is returned to the pressure station for reuse using liquid recovery and recycle system 40. In the pressure station, polymer 50 is contained within reservoir 51. Roller 12 rotates in the indicated direction so that its circumferential surface, preferably a textured or gravure surface, picks up liquid 50 from reservoir 51 and deposits it on the circumferential surface of roller 10 across a controlled width gap 13 between

rollers 10 and 12. Typically, gap 13 is actually less than the unencumbered thickness of the starting web 60. Roller 10 also preferably has a textured or gravure surface. Roller 10, rotating in the roller arrow indicated direction, which is opposite to the direction of travel of web 60, applies the polymer to one surface of the moving web 60, which is typically a fabric. Roller 11 is urged with a compressive force against the back or opposed surface of web 60 and roller 11 rotates in a direction which is the same as that in which web 60 travels. Roller 11 aids in achieving the desired pressured application of polymer into web 60 from the surface of roller 10.

Referring to Figure 6, the polymer is believed to be introduced into the web and into the interstices or open cells of the web 60 by the aid of a back-pulling or shearing action resulting from the distorting and pressuring of web 60 caused by rollers 10 and 11 rotating in the same direction. This direction may be the indicated direction with roller 10 rotating against the linear movement of web 60 indicated by web directional arrow 61, or all rollers 10, 11 and 12 may be reversed in respective rotational direction so as to cause each roll to turn in an opposite direction relative to that direction which is illustrated by the respective roller arrows in Figure 6. Regardless of which side of web 60 is back-pulled or subjected to shearing action by a reverse rotating roller, the web 60 is stretched and distorted to pull open the interstices of the web and to aid in forcing polymer 50 into the web 60. This distorting, and particularly this stretching, is believed to facilitate the full and deep introduction of the polymer into the moving web 60. However, it is to be understood that use of a reverse roll coater or other facilities which distort the web at the polymer application stage is not required. Other suitable polymer applicators well known in the art may be used to deposit the polymer on the surface of the web. Thereafter, the polymer may be shear thinned and placed into the web by use of one or more shear knives 20.

The extent of pressured application of the polymer 50 into the web 60 which occurs between rotating rollers 10 and 11 is controllable to some extent by such variables as the speed of roller rotation, the pressure exerted by rollers 10 and 11 on web 60, the durometer hardness and surface characteristics of each roll 10 and 11 (particularly of the preferred textured or gravure surface of roll 10). However, the pressurized application may also be carried out with rollers 10 and 11 which have finely milled, smooth circumferential surfaces. The viscosity of polymer 50 and the amount of polymer 50 transferred from roll 12 to roll 10 across gap 13 may also be varied to regulate controlled placement of polymer within the web. Feed roller 12 preferably rotates counter to application roller 10. The polymer 50 can be monitored to assure that its homogeneous composition is maintained. If desired, the polymer composition 50 can be altered to adjust to process needs during a continuous treating operation.

The result of the introduction of the polymer 50 into the web 60 which is accomplished between rollers 10 and 11 using a polymer composition 50, which can have the viscosity or consistency of a conventional bathtub caulk composition, is to produce a web 60, or fabric, whose interstices or open cells are substantially completely filled with polymer in the region of the internal layer, or to produce a web having its structural elements or fibers encapsulated, or to produce a web having a combination of an internal layer and encapsulated fibers. For

example, in the case of a fabric, the region of the internal layer can be such that spaces (i.e., interstices or open cells) between the fabric's fibers/filaments, or the fabric's yarn members (as the case may be) are filled with polymer 50. However, the amount of polymer 50 which is thus introduced into web 60 can be much less than a saturation level; for example, if desired, the amount introduced can be insufficient even to coat or substantially completely envelope individual fibers of the web. Actually, the polymer 50 can be relatively non-uniformly distributed in the web after such pressurized application. The action of the shear knife 20 in the next zone of processing is such as to smooth out and to make uniform the distribution of polymer 50 in web 60. Also, the shear knife 20 helps regulate the amount of polymer 50 that is allowed to remain in web 60. While one shear knife is shown, it may be desired use a plurality of such knives in sequence to provide a series of shear thinning stations.

After the shear zone, if desired, a top coat polymer can additionally be introduced; for example, just before or after a flex knife 30. By overcoating for example, the original polymer with a dilute or very thin second or top coat, a more tightly cross linked encapsulated or enveloped product may be achieved, or surface properties of the product can be varied or improved. For example, the top coating can comprise a dilute dispersion of a fluorochemical fabric treating composition. In a web treated therewith, such treatment enhances surface properties of the web, such as by increasing grease or chemical penetration resistance, or soil resistance, or the like. The dilute fluorochemical dispersion can be applied by spraying, misting, or the like. Both treating agents then enter a curing stage, which can be accomplished conveniently by passing the treated web through an oven wherein the temperature and web residence time are sufficient to cure both the fluorochemical and polymer compositions to a desired extent, or by radiation, if desired.

The amount of polymer composition actually introduced through the controlled placement, and into the preferably stretched openings of the interstices of the web 60 is influenced by such factors as the velocity of movement of web 60, the viscosity characteristics of polymer 50, the compressive pressure exerted by roll 10 against roll 11, the longitudinal tension exerted upon the tensioned web 60, the force of blade 20 against the web, the angle of blade 20 relative to the web, the number of shear blades used, the polymer distribution achieved by shear blade 20 and by scraper flex knife(s) 30, and the like. In particular, the polymer reintroduction and distribution believed to be achieved by bar or shear knife 20 is achieved by the exertion of a pressure against moving tensioned web 60. The shear force and the temperature elevation due to such shear force results in the polymer 50 flowing into the three-dimensional structure of the web 60.

Preferably, the polymer 50 is thixotropic. The flowing of the polymer 50 into the web 60 using controlled liquid rheology preferably does not result at the time of controlled placement in a fluid viscosity which is so low as to cause the impregnant to spread into and be distributed substantially uncontrolled throughout the web 60. However, the flowing activity of the polymer is preferably accomplished using a polymer 50 which has a controllable rheology and viscosity such that a polymer 50 will achieve a desired internal layer and/or envelopment of individual fibers of the web 60. Particularly when the web 60 is a fabric, this envelopment is

preferably a surrounding of the fabric's individual fibers with a localized layer or film of polymer while an internal layer is formed.

A plurality of web tension control devices 10 can be used in the region of metering bar or shear knife 20 and in the region of reintroduction scraper flex knives 30 along web 60 in order to provide the capacity for precision control of the tension exerted on web 60 and of the compressive pressures and shear forces exerted on web 60 at the metering bar or shear knife 20 and flexible knives 30.

As shown in Figure 6, the machine preferably includes an polymer 50 recovery and recycling system which more preferably also includes a filtering subsystem, such system being diagrammatically represented and indicated by line path 40. This system includes a collection tray, or pan, 41, positioned under and behind the moving web 60 to collect along the sides of web 60, the excess impregnating liquid as it is wiped from the web surface contacted by the shear knife 20 and/or by the recovery knives 30 and passed laterally into pan or tray 41. From the recovery collection tray 41, the excess polymer 50 is pumped back through a filter (not shown) into the reservoir 51 of the reverse roll coater for loading and distribution on the surface of roller 12, transfer to roller 10, and reapplication to portions of continuously moving web 60. The ability to reuse the excess polymer 50 wiped from the moving web 60 rather than losing such polymer within the process makes the entire process more economically attractive.

Another embodiment of a machine in accordance with this invention is shown schematically in side elevation in Figure 7. In this embodiment, rollers 10 and 11 of the Figure 6 methods and apparatus are replaced with a combination of a reservoir 51, and one or more bars or shear knives 100. A typical shear knife is illustratively shown in Figure 4b. For purposes of the apparatus shown in Figure 7, the knife shown in Figure 4b has a leading edge 250 and a trailing edge 260. The reintroduction bar or shear knife 100 shear thins the polymer 50 which is applied or deposited onto the moving web 60 from the reservoir 51 as a liquid or bath. The web 60 in effect constitutes a retaining wall for a part of the reservoir 51. The reservoir 51 thus functions to hold a pool of the polymer composition 50 against a surface of the moving web 60 which in the embodiment shown, is moving vertically upwardly. The bar or shear knife 100 functions to apply pressure or force upon the polymer composition polymer 50 that was deposited on the web 60, thereby to shear thin the polymer 50 and cause it to penetrate the web 60. The knife 100 also serves to distribute and move the polymer in the web and to accomplish envelopment of the fibers thereof. Excess polymer 50 is also scraped away by knife 100. Optionally, one or more of flexible or rigid knives 100 function to further reintroduce and distribute the polymer 50 and to envelope fibers of web 60 while forming an internal polymer layer within the web, or to produce a web having its structural elements or fibers encapsulated, or to produce a web having a combination of an internal layer and encapsulated fibers. The knives 110 can be considered to function in a manner which is equivalent to the knives 30 on the treated surface of web 50 in the Figure 6 methods and apparatus.

Typically, any polymer scraped from the moving web 60 by bar knife 100 falls directly back into the reservoir

51. Polymer scraped from the moving web 60 by scraper knife 110 is collected in sloping trough 120 and returned by falling along the indicated dotted line path to the reservoir 51. Longitudinal tension control of the moving web 60 is regulated by tension control devices 70 (such as a series of rollers) from a region beginning after reservoir 51 and extending to an oven 80 along the path of web 60 travel.

5 Relative to the Figure 7 embodiment, the Figure 6 embodiment is believed to exhibit a wider degree of control in the practice of the present controlled placement process. Particularly, both the initial applied amount and the successive pressurings of, a polymer 50 are precisely controllable. Relative to the Figure 6 embodiment, the Figure 7 embodiment is characterized by the capability for operation at higher web 60 transport speeds, typically at speeds characteristic of higher end commercial fabric finishing line operations. The embodiment shown in
10 Figure 6 is believed to be suitable for producing internally coated fabrics when the fabrics are of the thicknesses characteristic of garments, and where deeply controlled pressured placement over distances extending perpendicularly into and through a web of fabric greater than about 1/16 inch is not generally required.

Figure 12a depicts a schematic, side elevational view of another method and apparatus for practicing the present invention. In this method and apparatus, a continuous web 74 is moved along a web pathway from a supply roll
15 76 to a take-up roll 77.

In a first functional processing station 78, a polymer composition is applied to the upper face 79 of web 74 by a polymer applicator such as a conventional reverse roll coater 81. In the reverse roll coater 81, the polymer composition is applied to the surface of a reversely rotating (relative to the direction of travel of web 74) coating roll 82 from a nip region reservoir 83 formed between the coating roll 82 and a transfer roll 84 (which rotates in
20 the direction of travel of web 74, but whose surface does not contact web 74). The web 74 is transversely compressed between coating roll 82 and drive roll 86 as it passes through station 78. Thus, the polymer composition is applied under a positive pressure against face 79 by coating roll 82 which functions to cause the composition to be forced into web 74. A present preference is to use a coating roll 82 which has smooth, chrome plated surfaces. It is also possible to apply the polymer composition to the upper face 79 of the web 74 without
25 any force, leaving the controlled placement and shear thinning for a subsequent step or series of steps, such as by the force of the shear knives as described below.

Largely for purposes of controlling the alignment of web 74 with rolls 82 and 86, the web 74 is pretensioned by coating clutching rolls 87, 88 and 89. After the web 74 passes over guide roller 91 on the web pathway from supply roll 76, the web 74 passes over roll 87, between rolls 87 and 88, around roll 88, and between rolls 88 and
30 89. The clutching rolls 87, 88 and 89 are components of a conventional web clutching mechanism (not detailed) which provides for adjustments between rolls 87, 88 and 89 so that selective tensioning of web 74 is achieved along the web pathway between the clutching rolls 87, 88 and 89 and the nip region 92 defined between rolls 82 and 86 with the intervening roller roll 93 being used for guidance of web 74. The clutching rollers 87, 88 and

89 also function to smooth out and extend web 74 before it enters the coater methods and apparatus 81 so that in the methods and apparatus 81, the web will have polymer composition uniformly applied thereto.

After passing nip region 92 the web 74 is controllably longitudinally tensioned along the web pathway extending from nip region 92 to compensating and regulating coating tension rollers 94, 95 and 96. The tension rollers 94, 95 and 96 are components of a conventional web tension adjusting and regulating mechanism (not detailed) which provides for on-line, in-stream operator controlled adjustments between rollers 94, 95 and 96 that permit selective control of the tautness of web 74 particularly in the web pathway region from nip region 92 to rollers 94, 95 and 96. In the event a reverse roll coater is not utilized, the tension will be controlled in the region between rolls 87, 88 and 89 on one hand, and rolls 94, 95 and 96 on the other hand.

Along the tensioned web pathway region, the web 74 successively passes through each one or more of a series of processing stations 98, 99 and 100. While three processing stations are shown, more or less could be utilized in accordance with this invention. At each of the stations 98 and 99, a substantially non-flexible shear knife 101 and 102, respectively, extends laterally across web 74 with the web 74 being entirely unsupported on the lower face thereof which is opposed to upper face 79 and to the respective blades of each shear knife 101 and 102. A typical shear knife is illustratively shown in Figure 4b. For purposes of the apparatus shown in Figures 12a, 12b, and 12c, the knife shown in Figure 4b has a leading edge 250 and a trailing edge 260. Both to control the amount and type of shear force independently applied by each knife 101 and 102 the web 74 passes over each knife edge in a contacting relationship and three blade rolls 105, 106 and 107, that are provided in a typically fixed (but off-line adjustable) relationship relative to knives 101 and 102. The blades 101 and 102 are adjustable both vertically and angularly. By adjusting the vertical height of each blade relative to the web path, the force of each blade against the web can be controlled. By adjusting the vertical height of the blade rolls, the shear force can be controlled and the angle at which the web contacts the blades can also be controlled.

Relative to the direction of web 74 travel, blade rolls 105 and 106 thus are positioned so that roll 105 is on the lead side, and roll 106 on the trailing side, of knife 101 while blade rolls 106 and 107 are positioned so that roll 106 is on the lead side, and roll 107 is on the trailing side of knife 102. The angle of inclination or tilt of each blade 101 and 102 relative to the vertical is adjustable over a wide range, but it is presently preferred to adjust the blade inclination angle for each blade between about $\pm 45^\circ$ relative to the vertical with the web 74 being horizontal. In the embodiment shown, each respective blade is functionally associated with a knife back support or holder 108 and 109, respectively. Each support 108 and 109 permits its associated blade 101 and 102 to be vertically and angularly positioned relative to a supporting frame (not shown).

Another adjustable variable is the amount of angular web depression which, in the embodiment shown, extends downwardly, achieved by the web in its passage over the circumferential edges of adjacent rolls 105 and 106

relative to knife 101, and in its passage over the circumferential edges of rolls 106 and 107 relative to knife 102. Considering the place where the knife 101 or knife 102 contacts the web to be a hypothetical point, the angle of the knife 101 or knife 102 relative to the web can be in the range of about 30° to about 140°.

While it is presently preferred to employ shear knives 101 and 102 which have straight edges to shear thin the polymer composition, it will be appreciated that shear knives having somewhat curved edges can be used, if desired. For example, when treating a web which displays differential longitudinal stretch characteristics laterally thereacross in response to a uniform laterally applied warp tension, it appears to be possible to equalize the shear forces applied to a web by employing a suitably curved shear knife which appears to compensate for such a differential stretch characteristic.

- 10 While it is presently preferred to employ shear knives 101 and 102 which have sharp edges, shear knives can also be used which have dull or rounded edges. It is also preferred to use knives having edges which are surface finished to a uniformity of at least about root mean squared (RMS)8.

- 15 While it is presently preferred to employ shear knives 101 and 102 which are formed of steel, other materials of knife construction could be used if desired, such as metal alloys, non-metallic composites, and the like. The shear knives are preferably hardened or otherwise treated to reduce wear.

Those skilled in the art will appreciate that the amount of shear force applied by one or more shear knives 101 or 102 transversely against a web 74 is a function of many variables with probably the most important or principal variables being the polymer viscosity, the longitudinal web tension, and the positioning of the shear knives 101 and 102 relative to the web 74 during operation.

- 20 When a suitable and preferred level of applied shear force and web tensioning have been achieved to produce a product having encapsulated or enveloped fibers and/or an internal coating, or both, one can usually hear a distinctive sound in the region of a shear blade 101 and 102. This sound can also be heard in the vicinity of shear blades being used in the operation of other processes described herein. This sound can in fact be used by an operator as a rough guide as to whether or not the operator is succeeding in producing a product with controlled polymer placement containing enveloped fibers and/or an internal coating, or both.

Blade roll 105 also functions as a compensator roll for mechanically adjusting and controlling web tension before shear thinning begins. Also, conveniently and preferably the web tension is sensed electronically, and then roll 105 is automatically raised or lowered to achieve web tensioning adjustments so as to maintain a preset predetermined tension in web 74.

- 30 After passing over roll 107, the web 74 is passed over the circumferential surface of a conventional padder roll

111. Between the blade roll 107 and the padder roll 111, a flexible so-called "flex-knife" or "Spanish knife" 100 is positioned. Preferably, the blade of this flexible knife 100 is inclined at an angle with respect to the web 74 passing thereagainst so that the knife 100 exerts a compressive force against the face 79 of web 74 with opposed face 103 being entirely unsupported. The angle with respect to a (hypothetical) perpendicular line extending into a (hypothetical) straight line extending from the circumferential edge of roll 107 to the circumferential edge of roll 111 can range from about 30° to about 140° for the adjustment of the inclination angle of the flex knife. To provide adjustability for flexible knife 100, knife 100 is functionally associated with a mounting bracket or back support 113 which in turn is adjustable relative to an methods and apparatus frame (not shown).

In the embodiment shown in Figure 12a, the padder roll 111 is not employed as a web 74 treating means. It is not necessary to use the padder roll 111 in all applications. It is typically only used when tension is needed through the nip of the padder roll.

After leaving the mechanical tension compensator rolls 94, 95 and 96, web 74 is under reduced or preferably minimal tension and is led along a pathway which extends over spacer rolls 113 and 114. Alternatively, the web 74 may pass directly from the tension rolls 94, 95 and 96 into the curing oven 119. In the region over spacer rolls 113 and 114, and generally between tension roll 96 and idler roll 117, a platform 116 is conveniently positioned which can incorporate suitable instrumentation panels, operating controls and the like so that an operator can observe the operation of the apparatus in accordance with this invention and then control and regulate the same. A position which is suitable for operator observation of a web in progress that is located in the vicinity of a tenter frame 118 is desirable because it has been observed that a web being processed can experience some distortion owing to the forces exerted thereon. These distortions can be metered and observed and then the tenter frame 118 adjusted by the operator so that, as the web passes therethrough, the web can be straightened or shaped either longitudinally or laterally, as desirable or considered necessary for an individual web. If desired, the tenter frame 118 can be automatically operated to apply tensioning forces to a web in accordance with a predetermined program, or the like. It is to be understood, however, that a tenter frame may not always be necessary or desirable. Many webs may be processed in accordance with the principles of this invention without use of a tenter frame or other transverse tensioning device. In such cases, the web will pass directly into the curing ovens from the tension rolls 94, 95 and 96 or from the spacer rolls 113 and 114.

The tenter frame 118 also provides the start of a new zone of limited longitudinal and transverse tensioning which extends forwardly along the web pathway from tenter frame 118 through oven 119 to a tension compensator, here shown as utilizing three tension rolls 121, 122 and 123 which are part of a conventional mechanical tension compensator subassembly which is similar in structure and function to the compensator subassembly incorporating the previously described tension rolls 94, 95 and 96. The tensioning longitudinally of web 74 as it passes through oven 119 is employed to control the web 74 as it passes through oven 119 as regards web dimensional limits. This tensioning is chosen to be at a level which does not introduce significant distortion into

the web, yet web sagging is avoided, as from thermal expansion and elongation. Rollers (not shown) can be used in the oven 119 to avoid sagging and to maintain uniform heat exposure. It has been found for many applications that it is desirable to cure the treated web under substantially no tension. It is preferable that the web be cured in a relaxed state so that its original construction or the physics of its construction can be retained. This is instrumental for maintaining the correct hand and minimizing shrinkage.

In addition to serving as tension regulating means, the rolls 121, 122 and 123 also serve to provide a cooling pathway for the web 74 as it emerges from the oven 119 before it passes over guide roller 124 and onto take-up roll 77.

The oven 119 functions to cure the polymer composition selectively placed within the web 74. Oven 119 can be operated with gas or other energy source. Furthermore, the oven could utilize radiant heat, induction heat, convection, microwave energy or other suitable means for effecting a cure which are known in the art. Oven 119 can extend for from about 12 to about 20 yards.

Curing temperatures of from about 320° to about 500°F, applied for times of from about 2 minutes to about 30 seconds (depending upon the temperature and the polymer composition) are desirable. If a curing accelerator is present in the polymer, curing temperatures can be dropped down to temperatures of about 265°F or even lower (with times remaining in the range indicated).

In place of an oven, or in combination with an oven, a source of radiation can be employed (electron beams, ultraviolet light, or the like) to accomplish curing, if desired.

Less than the full heating capacity of the oven 119 can be used, if desired. For example, only top heating or only bottom heating with respect to the web can sometimes be used as compared to a combination of both top and bottom heating.

The take-up roll 77 is operating at approximately the same speed as the supply roll 76. When the rotational speeds of take-up roll 77 are not synchronized with rotational speeds of the supply roll 76, the tension roll combination of rolls 121, 122 and 123 can be used to take up or reduce web slack, as the case may be.

Web transport speeds can vary widely; for example, from about 2 yards per minute to about 90 yards per minute. Present speeds are from about 35 yards per minute to about 50 yards per minute.

The apparatus and processes described above can be used in various forms or embodiments. Referring to Figures 12b and 12c, two alternate variations or modes are seen. In such views, similar components are similarly numbered but with the addition of single prime marks thereto in the case of Figure 12b and double prime marks

thereto in the case of Figure 12c.

In Figure 12b, a further stage of web pressurization is introduced after the flex knife 112' and before the tenter frame 118'. Here, the web 74 after passage through the flex knife 112' is passed through the nip region 126 existing between padder roll 111' and associated transfer roll 127 where the web 74' is subjected to compression
5 between such rolls 127 and 111' for the purpose of achieving a better distribution of polymer composition on web 74.

After leaving nip region 126, the web 74 is retained under some compression against roll 127 by means of retaining bar or roll 128 for similar purposes. As discussed with reference to Figure 12a, the web 74 may pass directly into the oven 119' without utilizing the tenter frame 118'. It is desirable that the web curing start promptly
10 after tension is released in the nip region 126, thus it is preferred that the nip region 126 be located in close proximity to the entrance to oven 119'.

If desired, the roll 128 can be replaced by a flex knife (not shown) over whose edge the web 74' passes after departure from roll 127. The flex knife can accomplish substantial further polymer distribution in web 74.

Referring to Figure 12c, there is seen an embodiment where the web 74 is passed through the nip region of rolls
15 111" and 127". Here not only is use of the mechanical tension roll combination having rolls 94, 95 and 96 (as in Figure 12a) eliminated, but also the rolls 111" and 127" serve to end the region of high longitudinal tension in the stages of blade or knife application to web 74 and to provide the desired reduced tension for web passage through a curing station, here illustrated by oven 119" which may or may not use the intervening tenter 118".

Figure 14 depicts a schematic, side elevational view of a preferred embodiment or methods and apparatus for
20 practicing the present invention. In this embodiment a continuous web 302 is moved under tension along a web pathway from a supply roll 301 to a take-up roll 327.

The primary tension is a result of the differential rate between the driven entrance pull stand designated as 306 and the driven exit pull stand designated as 322, whereby the exit pull stand 322 is driven at a rate faster than the entrance pull stand 306. Other controllable factors which effect tension are the diameters of blade rolls 309, 314,
25 316, 318; the vertical depth of blades 311, 315, 317; the durometer of the entrance pull stand rolls 304, 305 and rubber roll 321 of the exit pull stand, and the friction as the web passes under the blades.

Web 302 passes between the nip of the two rolls 304 and 305 of the entry pull stand 306. The entry nip is adjustable to produce a force of from about 100 lbs. to about 5 tons on the web, passing between the two rolls. The weight of top roll 305 provides an even distribution of force throughout the web width. Web 302 is flattened
30 at this point and the interstitial spaces are reduced laterally and longitudinally. Bottom roll 304 has micro-

positioning capability to provide for gap adjustment and alignment. The top roll 305 composition is chosen based on the durometer of a urethane or rubber roll.

Web 302 continues to move along past idler roll 308 and blade roll 309 and forms an entry angle α and an exit angle β with blade 311. Blade 311 is illustratively shown in Figure 4b. For purposes of the apparatus of Figure 14, the blade in Figure 4b has a leading edge 250 and a trailing edge 260. Entry angle α can be varied by adjusting: (a) the height and diameter of blade rolls 309 and 314, (b) the horizontal position of blade rolls 309 and 314, (c) the angle of blade 311, and (d) the height of blade 311. Similarly, the entry and exit angles of blades 315 and 317, can be varied by adjusting the same devices surrounding each blade.

For illustrative purposes, increasing the height and diameter of blade roll 309 decreases entry angle α . Rotating blade 311 clockwise, with web 302 running left to right, increases entry angle α . Likewise, rotating blade 311 counter-clockwise, with web 302 running left to right, decreases entry angle α . Decreasing the distance between blade roll 309 and blade 311 decreases entry angle α . Increasing the downward depth of blade 311 into web 302 decreases entry angle α .

The angle of blades 311, 315, and 317 are completely changeable and fully rotational to 360°. The fully rotational axis provides an opportunity for more than one blade per rotational axis. Therefore, a second blade having a different thickness, bevel, shape, resonance, texture, or material can be mounted. Ideally the apparatus contains two or three blades per blade mount. The blade mounts are not shown.

The force or pressure of blade 311 applied against web 302 is determined by the vertical positioning of blade 311 in the blade mount. The greater the downward depth of blade 311, the greater the force or pressure. Blade pressure against the web is also accomplished through the tension of the web as described above.

The same line components that affect entry angle α , also affect exit angle β . Any changes in the height, diameter, or horizontal positioning of blade rolls 309 and 314, affects exit angle β . If the angle of blade 311 is rotated clockwise as described above, entry angle α increases, thus decreasing exit angle β .

As web 302 moves from left to right in Figure 14, polymer is deposited on web 302 with polymer applicator or dispersion means 310. Polymer applicator 310 can be a pump, a hose, or any available application device for applying polymer onto the surface of the web. Polymer applicator 310 is located directly in front of blade 311. The polymer is immediately shear thinned, placed into, and extracted from web 302 by the leading edge of blade 311, thus controlling the amount of polymer remaining in web 302. The bevel of blade 311 can effect entry angle α and the sharpness of the leading edge of blade 311. A sharper leading edge has a greater ability to push the weave or structural elements of web 302 longitudinally and transversely, increasing the size of the interstitial spaces. As the web passes the leading edge of blade 311, the interstitial spaces snap back or contract to their original size.

As web 302 moves from left to right in Figure 14, the process of shear thinning and placing polymer into and extracting it out of web 302 is repeated at subsequent blades 315 and 317, thus controllably placing the polymer throughout web 302. Web 302 then passes over idler roll 319 and between driven exit pull stand 322 which consists of rolls 320 and 321. Pull roll 320 is a driven roll proportionally driven at a predetermined rate slower than entry roll 304. Pull roll 321 does not apply pressure so much as it achieves a high degree of surface area in which web 302 must come into contact with. The larger the surface area, the higher the degree of contact friction. Pull roll 321 can be adjusted to have sufficient downward force to eliminate any slippage between web 302 and pull roll 320.

After web 302 passes from exit stand 322, it then moves into an oven 323 for curing. Rolls 324, 325, and 326 provide a tension regulating means and also serve to provide a cooling pathway for web 302 as it emerges from oven 323 before passing onto take-up roll 327.

The cure temperature of oven 323 is thermostatically controlled to a predetermined temperature for web 302 and the polymers used. Machine runs of new webs are first tested with hand pulls to determine adhesion, cure temperature, potentials of performance values, drapability, aesthetics, etc. The effect on web 302 depends on the temperature of oven 323, dwell time and curing rate of the polymer. Web 302 may expand slightly from the heat.

Oven 323 functions to cure the polymer composition that is controllably placed into web 302. Oven 323 can be operated with gas or other energy sources. Furthermore, oven 323 could utilize radiant heat, induction heat, convection, microwave energy or other suitable means for effecting a cure. Oven 323 can extend from about 12 to 20 yards, with 15 yards long being convenient.

Curing temperatures from about 320°F to about 500°F, applied for times of from about two minutes to about thirty seconds (depending on the temperature and the polymer composition) are desirable. If a curing accelerator is present in the polymer, curing temperatures can be dropped down to temperatures of about 265°F or even lower (with times remaining in the range indicated).

The cure temperature of oven 323 and the source and type of cure energy, are controlled for a number of reasons. The cure temperature of oven 323 is controlled to achieve the desired crosslinked state; either partial or full. The source and type of energy can also affect the placement of the polymer and additives. In place of an oven, or in combination with an oven, a source of radiation can be employed (electron beams, ultraviolet light, or the like) to accomplish curing, if desired. For example, by using a high degree of specific infrared and some convection heat energy for cure, some additives can be staged to migrate and/or bloom to the polymer surfaces.

Oven cure dwell time is the duration of time the web is in oven 323. Oven cure dwell time is determined by the speed of the oven's conveyor and physical length of the oven. If the dwell time and temperature for a particular

web is at maximum, then the oven conveyor speed would dictate the speed of the entire process line or the length of the oven would have to be extended in order to increase the dwell time to assure proper final curing of the web.

Take-up roll 327 is operated at approximately the same speed as supply roll 301. When the rotational speeds of take-up roll 327 are not synchronized with rotational speeds of supply roll 301, the tension roll combination of rolls 324, 325, and 326 can be used to reduce web slack.

Web speed is proportional to the variable speed of the motor which drives entrance pull stand 306 and exit pull stand 322. Web speed can effect the physics of the polymers as web 302 passes under blades 311, 315, and 317. Web transport speeds can vary widely; for example, from about two yards per minute to about ninety yards per minute.

- Typically, and preferably, webs of this invention are characterized by having fiber envelopment layers which range from about 0.1 to about 50 microns.

A presently preferred web which is both fluorochemical and silicone polymer treated and which is breathable, water resistant and rewashable is characterized as being a longitudinally tensionable porous flexible fibrous web having opposed substantially parallel surfaces that are comprised of associated fibers with interstices between the fibers, or is a matrix having cells or pores therein. The web is substantially uniformly impregnated with a fluorochemical and thereafter treated with a silicone polymer composition, to form a web having an internal layer within the web wherein the outer surfaces of the web are substantially free of silicone polymer and the web is breathable and water resistant or waterproof. At least a portion of the fibers or cell walls are encapsulated or enveloped. At least one surface of the web is characterized by having a visual appearance which is substantially the same as the visual appearance of one surface of the starting porous web.

When the web has fibers comprised of a synthetic polymer, the polymer is preferably selected from the group consisting of polyamides, polyesters, polyolefins, regenerated cellulose, cellulose acetate, and mixtures thereof.

Preferred webs of this invention are more specifically characterized by having a water drop contact angle in the range of about 90° to about 160°; a rewash capability of at least about 3; a breathability of at least about 35% of untreated substrate web; and a water repellency rating of at least about 80 prior to washing.

A general process for making a porous web of this invention comprises the steps of: tensioning a flexible, porous web as above characterized, applying a curable shear thinnable polymer composition to at least one web surface and then moving over and against one surface of the tensioned web a uniformly applied localized shear force to: shear thin the polymer composition, uniformly place the composition within the web, at least partially individually encapsulate or envelop surface portions of at least some of said fibers through the web matrix or position said

composition in a desired web internal region or some combination of both. Thereafter, the web is subjected to conditions sufficient to cure the composition in said web. Curing is accomplished by heat, by radiation, or both.

A presently preferred process for making a fluorochemical and silicone resin treated web having breathability, water resistance and rewashability which is adapted for continuous operation comprises the successive steps of:

- 5 impregnating the web with a fluorochemical, longitudinally tensioning the fluorochemical impregnated web while sequentially first applying to one surface thereof a curable silicone polymer composition and concurrently applying a transversely exerted localized compressive force against said surface, and moving over said surface of the web substantially rigid shearing means which exerts transversely an applied, localized shear force against said surface to shear thin the polymer and wipe away exposed portions of silicone polymer composition on said
- 10 surface, thereby forming an internal layer of silicone polymer and/or enveloping at least some of the fibers or passageways through the matrix, or both; and curing the silicone polymer composition in the web.

- The fluorochemical controlled placement operation is conveniently and preferably carried out by the steps of: substantially completely saturating the web with a solution or dispersion of a fluorochemical composition in a carrier liquid; compressing the saturated web to remove therefrom excess portions of said dispersion; and heating
- 15 said web to evaporate the carrier liquid therefrom. However, any convenient process can be used for accomplishing fluorochemical pretreatment of a web to be used in this invention.

The following text concerns the theory of the invention as it is now understood; however, there is no intent herein to be bound by such theory.

- The presently preferred polymer composition used in the treatment of webs by this invention is a non-Newtonian liquid exhibiting thixotropic, pseudoplastic behavior. Such a liquid is temporarily lowered in viscosity by high pressure shear forces.
- 20

- One aspect of the invention is a recognition that when high forces or sufficient energy are applied to curable polymer compositions, the viscosities of these materials can be greatly reduced. Conversely, when subjected to curing, the same liquid composition sets to a solid form which can have a consistency comparable to that of a hard elastomeric rubber. The internal and external rheological control of polymer materials achieved by the present invention is believed to be of an extreme level, even for thixotropes. When subjected to shear force, the polymer composition is shear thinned and can flow more readily, perhaps comparably, to water.
- 25

- The invention preferably employs a combination of: (i) mechanical pressure to shear thin and place a polymer composition into a porous web; (ii) an optional porous web pretreatment with a water repellent chemical, such as a fluorochemical, which is theorized to reduce the surface tension characteristics of the web and create a favorable surface contact angle between the polymer composition and the treated web which subsequently allows,
- 30

under pressure and shear force exerted upon an applied polymer composition, the production and creation of an internal coating or layer which envelopes fibers or lines cell walls in a localized region within the web as a result of polymer flow in the web or which encapsulates the fibers within the web; and (iii) a polymer composition impregnated preferably having favorable rheological and viscosity properties which responds to such working pressures and forces, and is controllably placed into, and distributed in a web. This combination produces a web having the capability for a high degree of performance. This product is achieved through pressure controlled placement and applied shear forces brought to bear upon a web so as to cause controlled movement and flow of a polymer composition into and through a web. Preferably, repeated compressive applications of pressure or successive applications of localized shear forces upon the polymer in the web are employed.

By the preferred use of such combination, a relationship is established between the respective surface tensions of the polymer and the web, creating a specific contact angle. The polymer responds to a water repellent fluorochemical pretreatment of the substrate so as to permit enhanced flow characteristics of the polymer into the web. However, the boundary or edge of the polymer is moved, preferably repeatedly, in response to applied suitable forces into the interior region of a porous web so as to cause thin films of the polymer to develop on the fiber surfaces and to be placed where desired in the web.

Thixotropic behavior is preferably built into a polymer used in the invention by either polymer selection or design or additive/filler design. For example, it now appears that thixotropic behavior can be accentuated by introducing into a polymer composition certain additives that are believed to impart enhanced thixotropy to the resulting composition. A lower viscosity at high shear rates (during application to a web) is believed to facilitate polymer flow and application to a web, whereas a polymer with high viscosity, or applied at a low shear rate (before and/or after application) actually may retard or prevent structural element (including fiber) envelopment or encapsulation.

Illustratively, the practice of this invention can be considered to occur in stages:

In stage 1, a silicone polymer composition impregnated is prepared. It can be purchased commercially and comes in typically two parts designated as A and B. For example, in a silicone polymer composition, as taught in U.S. Patent No. 4,472,470, a base vinyl terminated polysiloxane is the A part, while a liquid organohydrogensiloxane controlled crosslinking agent is the B part. Certain remaining components, such as a resinous organopolysiloxane copolymer and a platinum catalyst may (or can) apparently initially be in either part A or part B.

Stage 2 can be considered to involve the mixing of such a product's parts with or without additives. Changes in viscosity can be obtained and measured based on applied shear rates and shear stresses. Such changes can be experienced by a polymer with or without additives. Up to a 99% reduction in

viscosity of a liquid silicone polymer composition is believed to be obtainable by the shear forces involved in the shear thinning and forcing of a silicone polymer composition impregnant into a web. Thereafter, a very substantial increase in polymer viscosity is believed to be obtainable taking into account these same factors. Normally, the most significant factor is now believed to be the shear gradient that typically reduces the viscosity of the polymer below the starting or rest viscosity.

Stage 3 can be considered to be the pressure introduction stage. Up to a 99% reduction of the polymer viscosity is believed to be obtainable due to the applied shear forces, elapsed time, temperature, radiation and/or chemical changes. Thereafter, a significant increase or even more in the resulting polymer viscosity is believed to be obtainable. In this stage, partial curing of the polymer may take place. Most commonly, polymer viscosity is substantially decreased during the pressure controlled placement Stage 3 by the application of shear forces.

Stage 4 can be considered to be the first stage internal matrix dispersing and reintroduction with metering, and also recovery and recycle of excess polymer. Typically, within this Stage 4, the shear forces cause a substantial but temporary lowering of polymer viscosity, causing it to flow upon and into the three-dimensional structure of the web. The initial viscoelastic character of the polymer is typically theorized to be recovered almost immediately after shear forces are removed.

Stage 5 can be considered to be a second stage internal matrix dispersing and reintroduction with metering and also recovery and recycling of excess polymer. The variations in the viscosity of the polymer are equivalent to Stage 4. The viscosity of the polymer is again lowered causing it to flow within the web. Because of the application of repeated shear force induced reductions in viscosity, the thixotropic behavior of a polymer may not undergo complete recovery, following each application of shear force and the viscosity of the polymer may not revert to its original placement values. The polymer composition is believed to have the capacity to form enveloping internal coating in a predetermined region wherein the interstices or open cells are substantially completely filled within the three-dimensional matrix constituting a web during the time intervals that the is caused to flow under pressure in and about matrix components. In between these times, the polymer may recover substantially all of its initial high viscosity, although perhaps slightly less so with each repeated application of shearing pressure or force.

Stage 6 can be considered to be occurring just as curing is begun, and just as heat is introduced.

Stage 7 can be considered to be occurring with regard to the exertion of control of curing. Typically, at least a partial curing (including controlled cross-linking and/or polymerizing) is obtained by relatively low temperatures applied for relatively short times. For example, when light cotton, nylon, or similar

fabrics are being treated, temperatures under about 350°, applied for under about 10 seconds, result in partial curing.

Figure 8, consisting of Figures 8a through 8d, shows four graphs illustrating four ways that could be used for plotting polymer rheological behavior: (a) shear rate versus shear stress (uniform scales), (b) shear rate versus shear stress (log scales), (c) viscosity versus shear rate (uniform scales), and (d) viscosity versus shear rate (log scales), if desired, in the practice of this invention. Only the log versus log scales are believed to be capable of encompassing a full range of values for the three indicated variables. The graphs represent some broad ranges of viscosity changes relative to shear stress that could be undergone by a given silicone polymer composition during execution of a given pressured controlled placement procedure as taught herein.

- 10 For the purposes of the present invention, the term "surface tension" can be considered to have reference to a single factor consisting of such variables as intermolecular, or secondary, bonding forces, such as permanent dipole forces, induced forces, dispersion or nonpolar van der Waals forces, and hydrogen bonding forces. The strong primary bonding forces at an interface due to a chemical reaction are theorized to be excluded from surface tension effects; however, it is noted that even a small degree of chemical reactivity can have a tremendous influence on wetting effects and behavior affected by surface tension.

Surface tension is believed to induce wetting effects which can influence the behavior of a polymer composition impregnant relative to the formation of either a fiber enveloped layer therewith in a fibrous porous web, fiber encapsulation or both. For example, adhesion is theorized to be a wetting effect. Spontaneous adhesion always occurs for contact angles less than about 90°. However, for a combination of a rough surface and a contact angle over 90°, adhesion may or may not occur. In fact, roughness becomes antagonistic to adhesion, and adhesion becomes less probable as roughness increases.

Also, penetration is theorized to be a wetting effect. Spontaneous penetration occurs for contact angles less than about 90°, and does not occur for contact angles over about 90°. The roughness of a solid surface accentuates either the penetration or the repellency action, but has no influence on which type of wetting takes place.

- 25 In addition, spreading is theorized to be a wetting effect. Retraction occurs for contact angles over 90° or over planar surfaces for any contact angle. However, spontaneous spreading for contact angles less than 90°, especially for small contact angles, may be induced by surface roughness.

Figure 9 is a schematic vector diagram illustrating the surface tension forces acting at the vertex boundary line of a liquid contact angle on a planar solid surface. It illustrates how surface tension forces might be measured between a silicone polymer composition and a fiber of a web (or a fabric) as treated by the invention.

Figure 10 is a graph relating the contact angle over a smooth solid surface as a function of θ and i that apply respectively, to adhesion ($I \cos \theta + 1$), penetration ($i \cos \theta$), and spreading ($i \cos \theta - 1$).

Regions of adhesion versus abhesion, penetration versus repellency, and spreading versus retraction are shown by shaded areas. Figure 10 illustrates what is theorized to be the relationship of a silicone polymer composition to silicone polymer composition solids in a treated web as regards such factors as adhesion, penetration, spreading, and retraction.

Figure 11, consisting of Figures 11a through 11d, shows representative viscosity profiles plotted on log viscosity versus log shear rate graphs for (a) pseudoplastic flow, (b) dilatant flow, (c) pseudoplastic flow with superimposed thixotropic behavior, and (d) laminar Newtonian flow that erupts into turbulent flow at a critical transition point.

Figures 11a through 11d show a broad range of illustrative flow characteristics that could be demonstrated by silicone polymer composition impregnants suitable for use in this invention using pressured controlled placement of a web as taught herein.

For purposes of this invention, the term "wetting" is used to designate such processes as adhesion, penetration, spreading, and cohesion. If wetting transpires as a spontaneous process, then adhesion and penetration are assured when the solid surface tension exceeds the liquid surface tension. Surface roughness promotes these spontaneous wetting actions. On the other hand, no such generalizations can be made when the solid surface tension is less than the liquid surface tension.

Surface tension is measured as by S.T.L. units for liquid and by S.T.S. units for solids; both units are dyns/centimeter. When S.T.S. is less than S.T.L., then wetting is less ubiquitous and prediction of wetting behavior is more difficult. However, by taking advantage of the liquid/solid contact angle that forms when a liquid retracts over a solid, it is possible to calculate with reasonable accuracy the wetting behavior that can be expected. The reduction in liquid surface area can be computed in terms of the contact angle that the liquid makes with the solid surface. Contact angles are always measured in the liquid phase. There is a point of equilibrium where the surface tension forces become balanced.

By measuring the contact angle of a liquid on a solid, the wetting behavior of the liquid impregnant can be measured.

This invention is further illustrated by the following examples, which are not to be construed in any way as imposing limitations upon the scope thereof. On the contrary, it is to be clearly understood that resort may be had to various other embodiments, modifications, and equivalents thereof, which, after reading the description

herein, may suggest themselves to those skilled in the art without departing from the spirit of the present invention and/or the scope of the appended claims.

Examples:

EXAMPLE 1: *Liquid Silicone Polymer Preparation*

- 5 100 parts by weight of the curable liquid silicone polymer available commercially from Mobay as "Silopren® LSR 2530" was mixed in a 1:1 ratio, as recommended by the manufacturer. A Hockmayer F dispersion blade at low torque and high shear was used to do the mixing. To this mixture were added 5 parts by weight of BSF "Uvinul 400" and 5/10 parts by weight Dow Corning 7127 accelerator, believed to be a polysiloxane but containing an undisclosed active accelerated ingredient.

10 EXAMPLES 2-19: *Liquid Silicone Polymer Preparation*

The procedure of Example 1 was repeated with various other curable viscous liquid silicone polymer compositions commercially available. To this product system is added a substituted benzophenone and other additives, the result of which are shown in Table II . All parts are by weight.

Table II
Illustrative Silicone Resin Compositions

EX. NO.	STARTIN G SILICONE RESIN	MIXTURE RATIO OF PACKAGED COMPONENTS ¹	SUBSTITUTED BENZOPHENONE		OTHER ADDITIVES	
			NAME	PARTS	NAME	PARTS
1	Silopren® LSR 2530	1:1	Uvinul 400	5	7127 Accelerator	5/10
2	Silastic® 595 LSR	1:1	Uvinul 400	5	Syl-Off® 7611 ⁽²⁾	50
3	SLE 5100 Liquid BC- 10	10:1 1:1	Uvinul 400	5	Sylox® 2 ⁽³⁾	8
4	Silopren® LSR 2530	1:1	Uvinul 400	5	Hydral® 710 ⁽⁴⁾	10
5	Silopren® LSR 2530	1:1	Uvinul 400	5	Silopren® LSR Z3042 ⁽⁵⁾	1
6	SLE 5500	10:1	Uvinul 400	5		
7	Silopren® LSR 2540	1:1	Uvinul 400	5		
8	SLE 5300	10:1	Uvinul 400	5		
9	SLE 5106	10:1	Uvinul 400	5		
10	Silopren® LSR 2530	1:1	Uvinul 400	5	Flattening Agent OK412® ⁽⁶⁾	4
11	Silopren® LSR 2530	1:1	Uvinul 400	5	Nalco ⁽⁵⁾ 1SJ- 612 Colloidal Silica ⁽⁷⁾	50
12	Silopren® LSR 2530	1:1	Uvinul 400	5	Nalco® 1SJ- 614 Colloidal Alumina ⁽⁸⁾	
13	Silastic® 595 LSR	1:1	Uvinul 400	5	200 Fluid ⁽⁷⁾	7

14	Silopren® LSR 2530	1:1	Uvinul 400	5		
15	Silastic® 595 LSR	1:1	Uvinul 400	5	Zepel® 7040 ⁽¹⁰⁾	3
16	Silastic® 595 LSR	1:1	Uvinul 400	5	Zonyl® UR ⁽¹¹⁾	1/10
17	Silastic® 595 LSR	1:1	Uvinul 400	5	Zonyl® FSN- 100 ⁽¹²⁾	1/10
18	Silopren® LSR 2530	1:1	Uvinul 400	5	DLX-600® ⁽¹³⁾	5
19	Silopren® LSR 2530	1:1	Uvinul 400	5	TE-3608® ⁽¹⁴⁾	5

Table II Footnotes:

- (1) Ratio listed is that recommended by the manufacturer.
- (2) Syl-off® (registered trademark of Dow Corning) is a crosslinker.
- (3) Sylox® 2 (registered trademark of W.R. Grace Co.) is a synthetic amorphous silica.
- (4) Hydral® 710 (registered trademark of Alcoa) is hydrated aluminum oxide.
- (5) Silopren® LSR Z/3042 (registered trademark of Mobay) is a silicone primer (bonding agent) mixture.
- (6) Flattening Agent OK412® (registered Trademark of Degussa Corp.) is a wax coated silicon dioxide.
- (7) Nalco® ISJ-612 Colloidal Silica (registered trademark of Nalco Chemical Company) is an aqueous solution of silica and alumina.
- (8) Nalco® ISJ-614 Colloidal Alumina (registered trademark of Nalco Chemical Company) is an aqueous colloidal alumina dispersion.
- (9) 200 Fluid (registered trademark of Dow Corning) is a 100 centistoke viscosity dimethylpolysiloxane.
- (10) Zepel® 7040 (registered trademark of duPont) is a nonionic fluoropolymer.
- (11) Zonyl® UR (registered trademark of duPont) is an anionic fluorosurfactant.
- (12) Zonyl® FSN-100 (registered trademark of duPont) is a nonionic fluorosurfactant.
- (13) DLX-6000® (registered trademark of duPont) is polytetrafluoroethylene micropowder.
- (14) TE-3608® (registered trademark of duPont) is a polytetrafluoroethylene micropowder.

EXAMPLE 20: Internally Coated Fiber Encapsulated, Interstice Filled Fabric Preparation

A complete, stepwise, application of the inventive method in the production of an encapsulated fiber fabric was as follows.

The selected base fabric was TACTEL® (gold color) #612071 available from ICI Americas, Inc. through their

agent, Arthur Kahn, Inc. This fabric was 100% woven nylon. If desired, this and other fabrics may be calendered to modify surface texture. The fabric was weighed and measured. Its initial weight is 3.1 ounces per square yard. Its thickness equals 9 mils. The fabric was next washed with detergent, rinsed thoroughly, and hung to air dry. The fabric was soaked in water, wrung dry, and weighed. The water retained was equal to 0.8 g water/g fabric.

5 The fabric was then treated with a water repellent fluorochemical, a 2% solution by weight of Zepel® 7040. In order to do so the fabric must be soaked in a 2.5% solution of Zepel® water-repellent chemical in distilled water. This was because:

$$\frac{1 \text{ g fabric} * (0.02)}{0.8 \text{ g water}} = 0.025$$

The treated fabric was then run through a wringer and air dried. Next, the fabric was heated in an oven for 1 minute at 350°. This heating sinters the water repellent fluorochemical. The fabric with its fluorochemical residue is then run as in the Figure 7 embodiment, in a vertical configuration and is described below. The fabric is run from a roll that incorporates significant braking or clutching to initiate the tension required for controlled material alignment and coating during application. The fabric web travels through a series of idler rolls ending at the application trough. As it passes the application trough, it picks up a thin coating of silicone impregnant and then moves under a shear blade that is parallel to the floor. The silicone impregnant is applied at 1.0 oz./sq. yd.

15 and continues under a flex blade that is also parallel to the floor.

Multiple process stages of running the fabric with applied impregnant under the blades are preferably made. The multiple process stages are important, and are normally necessary. The impregnant is Mobay 2530 A/B in a 1:1 ratio and can be considered to be a viscoelastic liquid that flows only under the shear forces resulting from the pressured controlled placement. The impregnant is believed to return very substantially to its original viscous condition almost immediately upon release of the pressure. The impregnant was believed to flow a short distance within the matrix of the fabric during the short time that it was, because of pressure shearing forces, of lowered viscosity. Therefore, a number of "flows" may be usefully generated in a number of passes in order to properly distribute the impregnant in its preferred position substantially encapsulating the surfaces of the fabric's fibers.

20

Finally, the impregnated fabric was run through a line oven, of approximately 10 yards in length, at 4-6 yards per minute, and was cured at 325-350°F. It then passes through a series of idler rollers and is rolled up on a take-up roll, completing the tension zone. The resultant fabric has a non-tacky thin film of silicone that was internally coated to form a fiber encapsulated, interstice-filled layer in the fabric.

25

EXAMPLE 21: *Evaluation of Fiber Encapsulated Fabric Properties*

The test results of the original versus the produced fiber encapsulated fabric of Example 20 were as follows:

Table III

FABRIC	ORIGINAL FABRIC	ENCAPSULATED
Spray Rating (1)	20	100 (reverse=100)
Rain Test (2)	Fail	Pass
Abrasion Test (cycles) (3)	1,800	3,200
Moisture Penetration (4)	Saturated	0.0g
Hydrostatic Resistance (psi) (5)	1	2
MVTR (g/M ² /day)* (6)	4,414	2,362
Weight (oz/yd ²)	3.1	4.1

Amount Impregnated = 1.4 oz/yd²

*Environmental chamber at 104°F and 74% humidity.

Table IV

LAUNDERING TEST (Spray Ratings)	TIMES WASHED			
	Initial	5X	10X	15X
Impregnated Side	100	90	90	90
Reverse Side	100	90	90	90
Unimpregnated Treated Fabric	100	80	80	40

Accelerated Weathering Test (8)

Samples placed in QUV weatherometer for 72 hours.

Original= 7

Impregnated Side = 9

Reverse Side= 8

(1) The spray test was conducted in accordance with AATCC 22-1974. It measures water repellency of a fabric sample on a scale of 0-100, with a reading of 100 designating a completely water repellent fabric.

(2) The rain test was conducted in accordance with AATCC 35-1985. It measures resistance of a fabric sample to penetration of water under static pressure from a shower head of 3 feet/5 minutes. A fabric is stormproof when less than 1.0 gram of water is absorbed by a standardized blotter used in the test.

(3) The abrasion test was conducted in accordance with Federal Test Method Standard 191 A, Method

5306. Abrasion resistance is measured by mounting a fabric sample on a Taber Abraser Model 174 and measuring the number of cycles before the fabric begins tearing apart.

(4) The hydrostatic resistance test was conducted in accord with Federal Test Method Standard 191A, Method 5512. The test measures a fabric samples' resistance to water under pressure using the Mullen's Burst Test methods and apparatus. Test results are expressed in pounds per square inch at which water beads penetrate the fabric.

(5) The moisture vapor transmission (MVTR) test was conducted in accordance with ASTM E96-B. The test measures the amount of moisture vapor passing through a fabric sample in a controlled environment during a 24 hour period. The obtained MVTR figure is expressed in grams of water/square meter of surface/24 hour day. The environmental chamber was held at 104°F and 47% humidity.

(6) The moisture vapor transmission (MVTR) test was conducted in accordance with ASTM E96-B. The test measures the amount of moisture vapor passing through a fabric sample in a controlled environment during a 24 hour period. The obtained MVTR figure is expressed in grams of water/square meter of surface/24 hour day. The environmental chamber was held at 104°F and 47% humidity.

(7) A laundering test of the conventional household type was performed. Fabric samples were washed with Tide® detergent. There was no drying. A spray test was subsequently carried out after each wash to determine the effect of the washing.

(8) The accelerated weathering test was conducted in accordance with ASTM G-53. Samples of original and impregnated fabrics were placed in the weatherometer of QUV Company and results were compared. (All readings were based on a graduated color scale of 0-20; 10 designated the original color, while 0 designated a white out.)

EXAMPLE 22: *Description of Fabric Controlled Placement Through Scanning Electron Microscope (SEM) Photomicrographs*

Figures 3a, 3b and 3c were taken using a Cambridge 360 scanning electron microscope. The samples were cut using Teflon coated razor blades, mounted on 1/2 inch diameter aluminum stubs and coated with a gold/palladium alloy.

Figure 3a is a photomicrograph of the gold color Tactel fabric described in Example 20. The surface of the material has been magnified 120 times and shows that the cured silicone polymer impregnant is present as a thin film, or coating, or layer within the material and envelopes at least a portion of the fibers. The fiber bundles are

somewhat distinguishable in the weave, but each filament in the fiber bundles is not individually distinct.

The sample in Figure 3b has been magnified 600 times and shows the cross-section of a fiber bundle from the same Gold Tactel in Figure 3a. The cured silicone polymer impregnant envelopes at least a portion of the fibers. The interstices or void areas between filaments in the region of the internal coating are mostly filled or plugged by such impregnant. However, the web remains breathable and because of the impregnant barrier, is either water resistant or waterproof.

Figure 3c is the side of the fabric in Figure 1 opposite from which the silicone polymer impregnant was applied. The silicone polymer impregnant is most readily apparent at the fiber bundle interstices and not visible in the fiber bundles themselves.

10 EXAMPLE 23: *Fiber Enveloped Fabric Preparation*

The selected base fabric was Arthur Kahn TACTEL® (hot coral) #70146. This fabric is 100% nylon. The fabric was pretreated at Cal-Pacific (a commercial finisher of fabrics) with duPont ZEPEL® 6700. The impregnant composition is Mobay LSR 2530 A/B in a 1:1 ratio = 5% W UVINUL® 400 (5% of total weight of Mobay LSR). Controlled placement of this composition was performed in a three stage continuous process using equipment as shown in Figure 7 consisting of the following procedure:

The composition was applied to the fabric at (a) a pressure of 3 lbs./linear inch, utilizing (b) a shear (bar) knife at a high pressure, and at a 90° angle to the fabric (the edge of the knife is milled sharp). The rate of application is at approximately 1.0 oz./sq. yd. A flex knife was then applied at a 45° angle with the recovery system utilizing gravity. For both (a) and (b) above, the microweb pressure was applied at a low web speed on a roller system varied at from about 260-400 yards per hour. Next, the fabric is cured using an upper oven (lower oven turned off) at a temperature of about 320-330°F. The fabric was in the oven for approximately 3 to 4 minutes. The impregnant cures to a non-tacky thin film, as in the previous example.

EXAMPLE 24: *Prior Art Silicone Polymer Treated Fabric*

The fabric resulting from a prior art application of a viscous liquid curable silicone polymer composition is shown in Figure 2. The photographic view of Figure 2 is at 150X magnification. It shows a polyester and cotton cloth blend into which Dow Corning 590 LSR silicone polymer composition has been coated by a procedure of the prior art. The fabric side shown in Figure 2 is the top, or treatment, side, which was the fabric side upon which coating was accomplished.

As shown by the example of the treated fabric of Figure 2, the prior art impregnated fabric is characterized by

a high degree of disorder. A large number of particulates (typical) appear to litter the surface of the fabric. A substantial portion of the area of the surface, which appears to be a solid layer, is silicone polymer composition. Certain yarn fragments can be observed to protrude through the surface of this silicone polymer composition. Additionally, the silicone polymer composition on either the polyester or the cotton fibers, is not an encapsulation layer, but rather a matrix with the coated fibers being in general disarray, probably from forces occurring during the indicated prior art silicone polymer composition application procedure. Although silicone polymer composition is present upon the yarn or fiber surfaces of the substrate, and certainly is present as a layer upon the exterior surface of the three-dimensional fabric body, the silicone polymer composition has not controllably and individually encapsulated the fibers and left the interstices between fibers largely devoid of such polymer. In the prior art, a placement of silicone polymer composition in a fabric is not controlled to such a degree so as to produce a product in accordance with the present invention.

EXAMPLE 25: *Description of Fabric Controlled Placement Through Scanning Electron Microscope (SEM) Photomicrographs*

Figures 13a, 13b and 13c were taken using a Cambridge 360 scanning electron microscope. The samples are cut using Teflon coated razor blades, mounted on 1/2 inch diameter aluminum stubs, and coated with a gold/palladium alloy.

Figure 13a is a photomicrograph of the Tactel (Hot Coral) fabric described in Example 23. The surface of the material has been magnified 120 times and shows that the cured silicone polymer impregnant is present as a thin film, or coating, or layer within the material and envelopes at least a portion of the fibers. The fiber bundles are somewhat distinguishable in the weave, but each filament in the fiber bundles is not individually distinct.

The sample in Figure 13b has been magnified 800 times and shows the cross-section of a fiber bundle from the same Tactel in Figure 13a. The cured silicone polymer impregnant envelopes at least a portion of the fibers. The interstices or void areas between filaments in the region of the internal coating are mostly filled or plugged by such impregnant. However, the web remains breathable and because of the impregnant barrier is either water resistant or waterproof.

Figure 13c is the side of the fabric in Figure 1 opposite from which the silicone polymer impregnant was applied. The silicone polymer impregnant is most readily apparent at the fiber bundle interstices and not visible in the fiber bundles themselves.

Figure 15a depicts a 330 denier cordura fiber, encapsulated with a composite polymer, magnified 1950 times. The left side of the picture is in normal scanning electron mode and the right side of the picture is magnified 10 times in secondary electron microscopy back scatter mode. The isolated rectangular box image in the middle of

the left side was exposed to destructive electron beams isolated on the central opening in the center of the wrinkled formation. The wrinkled film casing represents the composite polymer (solid silicone and oxyethylated nylon) thin-film, this is a direct result of the destructive electron exposure. The image on the left side of the picture has surrounding fibers on the left and right side of the isolated fiber, which also has some wrinkled effects on the thin-film as a direct result of the destructive electron analysis. The rectangular box on the upper side of the picture was targeted for an elemental analysis. The electron beam was targeted at the rectangular box with very low current (10 KV and probe at 3.0 nA) to insure isolation of elemental signal from any other area. Figure 15b depicts the elemental graph of the targeted region, which clearly shows the presence of the composite polymer containing si or silicon. Combined, Figures 15a and 15b show fiber encapsulation by the composite polymer.

Figure 15c depicts a cut end of a filament illustrating a thin film encapsulation in white. A crack was created in the filament with a high temperature electron beam. This crack continues under the surface of the thin film. The filament has been cut and the thin film has been stretched or elasticized by the cutting of the filament. The two arrows in the upper right corner show the thickness or distance represented by the black box in the lower right corner as 126 nm.

Figure 15d depicts an isolated image on 330 Denier Cordura single filament fiber processed with the micro-finish fiber coating technology, magnified 5,720 times. The Bioengineered Comfort™ polymer containing engineered protein and solid silicone was used in the process with a moderate degree of shear. The image on top of the fiber is an undispensed protein polymer which clearly illustrates the presence of the protein after the micro-finish fiber coating process. The surface morphology has very small protein polymer particles encapsulated in the solid silicone polymer and is homogeneously dispersed throughout the film system on the fiber.

Figure 15e is an image of a white nylon magnified 178 times. The application side is shown at the bottom left hand corner of the image. The upper portion of the image is the non-application side. At the upper right corner is the intersection of the warp and fill fiber bundles, where the polymer presence can clearly be seen on the fibers. The internal layer of polymer that creates the liquid barrier or resistant property can be seen along the bottom right corner of the picture. This internal layer is a combination of polymer filling some interstitial spaces and polymer "glueing" together the fibers and filaments of the web.

Figure 15f is a Tunneling Electron Microscopy (TEM) image of a thin cross section of a filament encapsulated with polymer. The lighter image on the lower side of the frame is a polyester filament. The black spherical dots on the outer edge of the fiber are extremely dense processed material. In this imaging technique, the darker the image, the denser that specific material.

Figure 15g depicts an individual filament shown in a split screen format. The left hand image is showing the

filament with submicron metal particles dispersed in the processed film. The right hand portion of the split screen is imaging the filament with a technique known as secondary electron back scattering. The bright particles are the same particles on the same fiber as seen in the left side of the split screen. The difference is one of density, the brighter metal particles are imaging density differential over the underlying filament.

5 Figure 15h depicts a nylon fabric magnified 419 times with bright particle tracer images and a cross sectional image of a nylon fabric. These bright particles are submicron metal particles dispersed throughout the fabric in the processed film. The addition of bright copper submicron particles in the polymer allows secondary back scatter mode to illustrate the complete encapsulation ability of the controlled placement technology. The left side of the image is the performance side of the fabric which is the non-application side of the polymer, but it is clear, with the presence of the glowing brightness of the copper submicron particles throughout the performance side of the fabric, that controlled placement technology successfully encapsulates completely around the fibers throughout the fabric structure. The other clear unique feature of the controlled placement technology is that each fiber is still independent. This differentiation allows the controlled placement technology's processed fabrics to retain exceptional hand and tactile quality, while still imparting performance characteristics. On the left side of the fabric, directly underneath the printed text "performance side", an elemental analysis was conducted and the outcome of that analysis is depicted in figure 15i. The result clearly shows a strong presence of submicron copper particles.

In the next examples that involve accelerated weathering, abrasion, water repellency, moisture penetration, and rain testing, data is provided for a Tactel fabric identified as Deva Blue. The fabric is 100% nylon, available from Arthur Kahn and identical in composition, preparation, and enveloping specification to that of the Hot Coral presented in previous examples.

EXAMPLE 26: *Accelerated Weathering Test*

The results of weathering upon a treated web of this invention are shown in actual tested sample pieces comparing original fabrics with embodiments of the enveloped fiber fabrics of this invention.

In every case, the enveloped fiber fabric samples were found to have significantly better weathering characteristics than the original untreated fabrics as determined by accelerated weathering tests. Even the reverse side (compared to the treated side) of an enveloped fiber nylon fabric of the Tactel® type was improved over the original fabric. In addition, the excellent "hand" of the enveloped fiber fabric was found to have been maintained after the accelerated weathering test.

The test performed conforms to each of the following performance standards:

- ASTM G-53 light/water exposure materials

- ASTM D-4329 light/water exposure-plastics
- General Motors Test spec TM-58-10
- ISO 4892 Plastics exposure to lab light

The procedure used for the accelerated weathering testing involved subjecting fabric samples to four hours of high-intensity ultraviolet light, alternating continuously with four hours of water condensation, wetting the fabric in the dark. This alternating exposure (four hours on, four hours off) to high-intensity ultraviolet light and water wetting, simulates outdoor environmental conditions in a vastly accelerated manner, quickly degrading unprotected dyes and fibers. The methods and apparatus used for this test was a QUV Accelerated Weathering Tester from The Q-Panel Company, 26200 First Street, Cleveland, Ohio 44145.

The results obtained on some sample fabrics are expressed in Table V. In this Table, results are expressed in the form of "A/B" where A and B are numbers. The number "A" is the color rating on a graduated scale from 0 to 10. The number 10 equals perfect (original) condition where 0 equals a white color and a completely faded fabric. The number "B" is the number of hours of weathering transpiring when the number "A" rating was obtained.

Table V
Accelerated Weathering Testing

ORIGINAL FABRIC	ORIGINAL FABRIC WEATHERED	ENVELOPED FABRIC WEATHERED	REVERSE SIDE WEATHERED	COLOR RATING (RATING/HOURS) 10 - PERFECT 0=WHITE FADES OUT
TACTEL° Deva Blue 9-420-6-1 10/0	3/159	8/159		After 159 hrs., enveloped fabric significantly less weathered than original; original nearly white; enveloped fabric still light blue.
TACTEL° Hot Coral 9-420-6-2 (AKA 18) 10/0	5/24	10/24	9/24	After 24 hrs., enveloped fabric is significantly less weathered than original, as was reverse side.

EXAMPLE 27: *Abrasion Resistance Testing*

The results of abrasion resisting testing clearly show that enveloped fiber fabrics of this invention have superior wear characteristics compared to the untreated original (starting) fabrics. In most cases, the enveloped fiber fabric samples underwent twice as many cycles as the untreated samples without evidencing tearing in the samples.

- 5 Such results can be explained by theorizing that the envelopment with silicone polymer of the yarns and fibers comprising a fabric, provides such treated yarns and fibers with a lubricity agent so that abrasive action was minimized and the integrity of the fabric was preserved significantly longer. The anti-abrasion characteristics also applied to the minimized effects of one fiber rubbing against another fiber, or of one yarn against another yarn.

- 10 This experiment compared the abrasion resistance of embodiments of the enveloped fiber fabrics of this invention with untreated fabrics. The durability of each fabric test specimen was determined by the Taber Abraser. Each specimen is abraded for the number of cycles indicated. Comparisons were then made between the enveloped fiber fabrics of the invention and untreated fabrics. Specifically, this test method utilizes the Taber Abraser No. 174. An important feature of this abrader was that its wheels traverse a complete circle on the test specimen surface. Thus, the surface was abraded at all possible angles relative to the weave or grain of the specimen.
- 15 Comparisons of the enveloped fiber fabric to the untreated fabric were based upon a scale 0 through 10, where 0 was a completely torn specimen, and 10 was the new (or starting) sample.

Each test procedure used a single 7 inch diameter fiber enveloped fabric specimen, and a single 7 inch diameter original (untreated) fabric specimen. The procedure used was as follows:

- 20 1. A test specimen of the fiber enveloped fabric with a 7 inch diameter was cut.
2. An equally-sized specimen of control (untreated) fabric was cut.
3. The fabric specimen was mounted on the rotating wheel securely and the clamps were screwed down.
4. The counter was set.
5. The vacuum power adjustment was set. (For this experiment, vacuum was set at 80.)
- 25 6. The abraser was started.
7. At the procedurally specified number of revolutions, the abraser was stopped and each fabric sample was rated at a value between 0 and 10.

Illustrative results of the test on some sample fabrics are shown in Table VI.

Abrasion Testing

Numeric Grade of Abrasion 0 - 10

- 0 - Total failure of fabric specimen. Fibers are torn apart
- 5 - Fabric specimen is starting to tear. Fabric is noticeably thinner
- 10 - Original unabraded fabric specimen

Table VI

SPECIMENS	UNTREATED FABRIC	ENCAPSULATED FABRIC	COMMENTS
Hot Coral Tactel	5 1,000 cyc.	7 1,000 cyc.	Untreated sample is starting to tear, and enveloped sample was still intact.
Deva Blue Tactel	4 1,000 cyc.	7 1,000 cyc.	Visible rips in untreated sample. Enveloped sample fibers were frayed.

10 EXAMPLE 28: *Breathability Testing*

This test procedure followed the Modified ASTM E96-8 test. As shown by the results of this testing in the following Table, the fiber enveloped fabrics of this invention were found to have high breathability. This breathability was in excess of that needed to remove the average value of several thousand grams of perspiration generated daily by the human body. The results for the fiber enveloped fabrics of this invention were generally superior to the corresponding results measured under the same conditions for prior art treated fabrics, such as the Gore-Tex® brand fabric.

Breathability of a fabric sample was determined by accurately weighing the amount of water passing through such fabric sample under carefully controlled temperature and relative humidity conditions in an environmental chamber. The water weight loss from a cup whose mouth is sealed with a fabric sample was expressed as grams of water vapor per square meter of fabric per 24 hour day.

In an attempt to more realistically simulate what is actually occurring inside the apparel during exercise, a specially designed test was performed to measure outward water vapor transport (MVTR) in a "Bellows" effect. The test simulates the high volumes of moisture and air that mix within a garment that pass outward through it as air is drawn in resultant from activity. The enveloped fabrics of this invention were found to provide increased performance at a higher activity, or air exchange level than is achievable with corresponding untreated fabrics.

The "Bellows" MVTR breathability test was run inside of a controlled temperature/humidity chamber similar to the foregoing cup test. However, instead of a standard cup, each fabric sample was sealed over the open top of a special cup which was provided with an air inlet aperture in its bottom, thereby allowing air to be bubbled up through the sealed container at a controlled rate. A check valve at the air inlet operation prevents backup or loss of water from the container. The air bubbles passed upwardly through the water and out through the fabric sample mounted sealingly across the cup top along with the water vapor. Table VII illustrates some representation results obtained.

Table VII
Moisture Vapor Transport (MVTR)

FABRIC	MVTR ⁽¹⁾
Made by a Method of the Invention	
Enveloped fiber fabric, Hot Coral Tactel®	13,600
Commercial Products	
Gore-Tex\3-Ply Fabric	10,711

Table Footnote:

- (1) MVTR here references moisture vapor transport through a fabric sample as measured by the "Bellows" test with air delivered to the bubbler at 2 to 4 psi air pressure, in an Environmental Chamber at 100 to 102°F and 38 - 42% relative humidity. MVTR is expressed as grams of water per square meter of surface per 24 hour day.

EXAMPLE 29: *Water Repellency: Spray Testing*

Water repellency spray testing is carried out according to AATCC Test Method 22-1974. The results of such testing show that the fiber enveloped Tactel®-type fabrics of the invention show excellent initial spray ratings initially, as do the original untreated fabrics which have been treated with water repellent chemicals such as fluorochemicals. Specifically, as the results shown below demonstrate, after ten machine washes, the treated side of a fiber enveloped fabric of the invention was found to remain highly water repellent, while, on the reverse side thereof, the original water repellency rating was found to have fallen significantly. The water repellency spray rating on the untreated fabric fell even more drastically. Excellent "hand" was retained after the test. It is believed that pretreatment with a fluorochemical having good water repellent properties can augment and even synergistically coact with the silicone resin used to produce fiber enveloped fabrics of this invention to produce superior spray ratings in such a fiber. The results are shown in Table VIII.

This test method is believed to be applicable to any textile fabric, whether or not it has been given a water resistant or water-repellent finish. The purpose of the test is to measure the resistance of fabrics to wetting by

measuring the water-repellent efficiency of finishes applied to fabrics, particularly to plain woven fabrics. The portability and simplicity of the instrument, and the shortness and simplicity of the test procedure, make this method of test especially suitable for mill production control work. This test method is not intended, however, for use in predicting the probable rain penetration resistance of fabrics, since it does not measure penetration of water through the fabric.

The results obtained with this test method are believed to depend primarily on the resistance to wetting, or the water repellency, of the fibers and yarns comprising a fabric, and not upon the construction of the fabric. This test involves spraying water against the taut surface of a test fabric specimen under controlled conditions which produce a wetted pattern whose size depends on the relative water repellency of the fabric. Evaluation is accomplished by comparing the wetted pattern with pictures on a standard chart. The methods and apparatus and materials employed for this test were an AATCC Spray Tester, a beaker, distilled water, and the specimen fabrics.

The procedure followed for this test was as follows: a test specimen, which had been conditioned as procedurally directed, was fastened securely in a 15.2cm (6") metal hoop so that it presented a smooth wrinklefree surface. The hoop was then placed on the stand of the tester so that the fabric was uppermost in such a position that the center of the spray pattern coincided with the center of the hoop. In the case of twills, gabardines, piques or fabrics of similar ribbed construction, the hoop was placed on the stand in such a way that the ribs were diagonal to the flow of water running off the fabric specimen.

250 milliliters (ml) of distilled water at $27^{\circ}\text{C} \pm 1^{\circ}\text{C}$ ($80^{\circ}\text{F} \pm 2^{\circ}\text{F}$) was poured into the funnel of the tester and allowed to spray onto the test specimen, which took approximately 25 to 30 seconds. Upon completion of the spraying period, the hoop was taken by one edge and the opposite edge tapped smartly once against a solid object, with the fabric facing the object. The hoop was then rotated 180 degrees and then tapped once more on the location previously held.

The procedure and methods and apparatus of this test were slightly modified from the specifications, as follows:

1. The spray nozzle holes were slightly larger than specified, but the flow rate of the nozzle was 250 ml/30 sec., as required.
2. The number of taps of the hoop was two instead of one.

For each wash test, a fabric sample was washed using a warm wash/cold rinse cycle with one cup of Tide® detergent and dried at a hot/dry cycle in a dryer, unless otherwise indicated. The test results were evaluated by comparing the wet or spotted pattern on the fabric sample after tapping the hoop with the standard rating chart.

Results produced surface wetting, with no water completely soaking through the test fabric sample. The numbers

were ratings based upon the standard chart. Such values are thus subjective deductions by an experienced experimenter.

Table VIII
Spray Test Results

ORIGINAL FABRIC	ENVELOPED FIBER FABRIC OF THE INVENTION							
	Initial				After 5 Washes		After 10 Washes	
	Initial	After 4 Washes	Enveloped Side	Reverse Side	Env. Side	Reverse Side	Env. Side	Reverse Side
Deva Blue 9-420-6-1	100	10	90	100	90	70	80	50
Hot Coral 9-420-6-2	100	30	90	100	70	55	70	30
Gold Tactel 8-100-1	100	100	90	90	90	90	90	90

EXAMPLE 30: *Moisture Penetration Test*

The results shown in the Table below demonstrate that all of the fiber enveloped fabrics of this invention test were significantly better than the original untreated fabrics with regard to resisting the penetration of water under the test conditions used after the test, the "hand" of the tested fabric samples remained excellent

The purpose of this test was to evaluate how well a fabric stands up to wetness under continuous pressure, such as kneeling on the ground, or sitting in a wet chairlift, for a period of 30 minutes. This test involves placing both a fabric sample and a standard blotter sample on top of a water container which contains 700 ml of tap water. The fabric sample and the blotter sample are each then subjected to a continuous pressure of 87 lbs. distributed evenly over 100 square inches of surface area for a period of 30 minutes. After this time, a visual inspection of the fabric is made for any water penetration, and the paper blotter is weighed to detect water gain or penetration.

The methods and apparatus employed for each such test was one 20 inch diameter aluminum pan, one 87 lbs. weight distributed evenly over 100 square inches of fabric, one paper blotter, 700 ml water, miscellaneous fabric scraps for cushioning and the test fabric sample pieces.

■ Paper blotter dry weight: 4.7 gm

- Total weight applied to fabric: 87 lbs.
- Pressure evenly distributed over surface area of: 100 sq. in.
- Pressure: 0.87 lbs./sq.in

5 The procedure observed for this test was as follows:

1. 700 ml tap water was placed in the round pan.
2. The fabric sample was placed with one side facing the water.
3. One piece of dry blotter paper was placed over the fabric to cover the pan.
4. Scrap fabric was placed over the blotter paper to cushion the weight.
- 10 5. The 87 lb. weight was distributed evenly over the 100-square-inch area.
6. This assembly was left undisturbed for 30 minutes.
7. After this time period, the visual results were recorded.

Table IX

Fiber Enveloped Fabric of the Invention

FABRIC SAMPLE AND THICKNESS	ENVELOPED SIDE OF FABRIC FACING WATER	NON-ENVELOPED SIDE OF FABRIC FACING WATER	CONTROL FABRIC
Deva Blue Tactel® 0.009 microns	No water penetration through the fabric. No visible water spots. Paper weight=4.7 gm Water gain=0.0 gm	No water penetration through the fabric. No visible water spots. Paper weight=4.7gm Water gain=0.0gm	Failure - total saturation of fabric and blotter.

EXAMPLE 31: *Rain Test*

In this testing, the rain test procedure of AATCC Method 35-1985 was followed.

The rain test results obtained demonstrate the clear superiority of the fiber enveloped fabric of the present invention as compared to the original untreated fabric. The data in the Table below shows that fiber enveloped fabrics pass this test by allowing virtually no water to pass therethrough. This result is comparable to the results obtained with higher cost so-called breathable waterproof fabrics currently commercially available in the market. In contrast, the original, untreated fabrics fail to pass this test because they demonstrate complete saturation. The fiber enveloped fabric samples retain excellent "hand" after the test.

The purpose and scope of this ASTM test is to evaluate resistance of a fiber enveloped fabric to water under simulated storm conditions. The test specifies that a test fabric is stormproof if less than one gram of water is absorbed by blotter paper with a shower head pressure of 3 feet exerted for 5 minutes. This test method is applicable to any textile fabric, whether or not it has a water repellent finish. It measures the resistance of a fabric to the penetration of water by impact, and thus can be used to predict the probably rain penetration resistance of a fabric. The results obtained with this method of test depend on the water repellency of the fibers and yarns in the fabric tested, and on the construction of the fabric.

This test involves a test specimen backed by a pre-weighed standard blotter. The assembly is sprayed with water for 5 minutes under controlled conditions. The blotter then is separated and weighted to determine the amount of water, if any, which has leaked through the specimen fabric during the test and has been absorbed by the blotter.

The methods and apparatus and materials employed in each test were a modified rain tester, blotter paper, water at $80^{\circ}\text{F} \pm 2^{\circ}\text{F}$, a laboratory balance, 8" x 8" fabric specimens which had been pre-conditioned in an atmosphere of 65% ($\pm 2\%$) relative humidity and $70^{\circ}\text{F} (\pm 2^{\circ}\text{F})$ for four hours before testing, and tape.

The procedure followed for this test was as follows:

1. A 6" x 6" paper blotter was weighted to the nearest 0.1 gm and placed behind the test specimen.
2. The test fabric with the paper blotter in registration therewith was taped on the specimen holder.
3. A tube in the rain tester was filled with water up to the 3 foot level. It was confirmed that water was flowing out of the overflow tube which maintains the 3 foot column of water.
4. The water spray distance from the tip of the nozzle to the specimen holder was measured and adjusted to 12 inches.
5. The specimen holder was left in place and the rain tester was turned on for five minutes.
6. After the test period, the paper blotter was removed and reweighed to the nearest 0.1gm.

The results of the test selected fabric samples are shown in Table X.

Table X

Rain Test: Grams of Water Penetrating the Fabric

FABRIC SAMPLE	ORIGINAL NOT WASHED	AFTER 5 MACHINE WASHES	AFTER 10 MACHINE WASHES
Hot Coral Tactel°	0	0	0
Deva Blue Tactel°	0	0	0
<u>Prior Art Treated Fabrics</u>			
Ultrex°	0	-	0.1
Gore-Tex°	0	0	-

Original Fabrics - Water Repellant Chemicals Only. No Encapsulation

10 Hot Coral Tactel/Failed-saturated; Deva Blue Tactel/Failed-saturated

It should be understood, of course, that the foregoing relates only to preferred embodiments of the present invention and that numerous modifications or alterations may be made therein without departing from the spirit and the scope of the invention as set forth in the appended claims.

CLAIMS:

What is claimed is:

1. Apparatus for controlling the placement of a polymer composition into a porous web having a plurality of structural elements with interstitial spaces therebetween comprising:
5 means for applying tension to the porous web;
means for applying a curable, shear-thinnable, polymer composition onto a surface of the tensioned web;
and
means for shear thinning the polymer composition to substantially reduce its viscosity and selectively placing it into the tensioned web, leaving at least some of the interstitial spaces open.
- 10 2. Apparatus as set in forth in Claim 1 wherein said polymer composition is selectively placed to encapsulate at least some of the structural elements of said web.
3. Apparatus as set forth in Claim 1 wherein said polymer composition is selectively placed as an internal layer within said web positioned in a region extending through the web in a direction generally spaced from at least one major surface of said web.
- 15 4. Apparatus as set forth in Claim 1 wherein said polymer composition is selectively placed to encapsulate at least some of the structural elements of said web and to form an internal layer within said web in a region extending through the web in a direction generally spaced from at least one major surface of said web.
- 20 5. Apparatus as set forth in Claim 1 wherein the means for shear thinning and placing comprises a blade urged against the surface of the tensioned web downstream of the position where the polymer composition is applied to the web.
6. Apparatus as set forth in Claim 1 wherein the means for shear thinning and placing comprises two or more blades spaced apart from one another and urged against the surface of the tensioned web.
7. Apparatus as set forth in Claim 6, including means for controlling the spacing between said blades.
- 25 8. Apparatus as set forth in Claim 5 wherein said blade is positioned perpendicularly to said moving web.
9. Apparatus as set forth in Claim 5, including means for varying the angle of said blade relative to said web.

10. Apparatus as set forth in Claim 5, including means for controlling the force of said blade against said web.
11. Apparatus as set forth in Claim 5 including means for advancing the web past said blade.
12. Apparatus as set forth in Claim 11, including means for varying the exit angle of the moving web relative to said blade.
13. Apparatus as set forth in Claim 11 including means for varying the entrance angle of the moving web relative to said blade.
14. Apparatus as set forth in Claim 11 including means for varying both the entrance angle and the exit angle of said moving web relative to said blade.
- 10 15. Apparatus as set forth in Claim 6, including means for advancing the web past said blades.
16. Apparatus as set forth in Claim 15, including means for varying the exit angle of the moving web relative to said blade
17. Apparatus as set forth in Claim 15, including means for varying the entrance angle of the moving web relative to said blade.
- 15 18. Apparatus as set forth in Claim 15, including means for varying both the entrance angle and the exit angle of said moving web relative to said blade.
19. Apparatus as set forth in Claim 15, including means for independently controlling the force of each of said blades against said moving web.
20. Apparatus as set forth in Claim 1, including means for controlling the tension of the web.
- 20 21. Apparatus as set forth in Claim 1, including means for scraping the excess polymer from the surface of the web.
22. Apparatus as set forth in Claim 1 including means for curing the polymer composition within the porous web.
23. Apparatus as set forth in Claim 22, including means for controlling the temperature of the curing means.

24. Apparatus as set forth in Claim 22, wherein said curing means comprises a curing oven.
25. Apparatus as set forth in Claim 5, including means for controlling the temperature of said blade.
26. Apparatus as set forth in Claim 6, including means for controlling the temperature of each of said blades.
27. Apparatus as set forth in Claim 5, including means for cooling said blade to prevent premature cure of
5 the polymer composition.
28. Apparatus as set forth in Claim 6, including means for cooling said blades to prevent premature cure of said polymer composition.
29. Apparatus as set forth in Claim 11, wherein said advancing means comprises a pair of counter-rotating nip rolls.
- 10 30. Apparatus as set forth in Claim 29, including means for controlling the pressure between said nip rolls.
31. Apparatus as set forth in Claim 29, wherein one of the nip rolls has a rubber surface of a predetermined hardness.
32. Apparatus as set forth in Claim 29, wherein both nip rolls have a rubber surface of predetermined hardness.
- 15 33. Apparatus as set forth in Claim 5, including means for damping the resonance of said blade.
34. Apparatus as set forth in Claim 6, including means for damping the resonance of said blades.
35. Apparatus as set forth in Claim 5, including means for vibrating said blade.
36. Apparatus as set forth in Claim 5, including means for vibrating said blade at a predetermined frequency.
37. Apparatus as set forth in Claim 6, including means for vibrating said blades.
- 20 38. Apparatus as set forth in Claim 6, including means for vibrating said blades individually at predetermined frequencies.
39. Apparatus as set forth in Claim 5, wherein said blade has a flat surface at the bottom thereof.

40. Apparatus as set forth in Claim 39, wherein the angle of entry of the web into said blade is greater than 0 degrees and less than 90 degrees, the web follows the bottom surface of said blade and the angle of exit of the web from said blade is greater than 0 degrees and less than 90 degrees.
41. Apparatus as set forth in Claim 1, including means for applying the polymer composition to the other side of said web, and means for shear thinning and selectively placing the polymer composition into said web from the other side of said web.
42. Apparatus as set forth in Claim 22, including means for controlling the release of longitudinal tension of said web to cause the structural members to separate prior to cure.
43. Apparatus as set forth in Claim 22 wherein said web is under substantially no tension during curing.
44. Apparatus as set forth in Claim 25 including means for holding said web under transverse tension during curing.
45. Apparatus as set forth in Claim 1 including means for distorting the web during shear thinning to facilitate entrance of the polymer composition within the web.
46. Apparatus as set forth in Claim 45 wherein said means for distorting comprises means for stretching said web transversely.
47. Apparatus for controlled placement of a polymer composition into a porous web comprising:
means for advancing a web and applying longitudinal tension;
means for applying a polymer composition of viscosity greater than 5,000 centipoise onto the surface of said moving web; and
means for shear thinning the polymer composition and controlling the depth and placement of the polymer composition within the web and for removing excess polymer composition from the surface of the moving web.
48. Apparatus according to Claim 47 wherein the means for shear thinning and controlling comprises:
a blade urged against the advancing web; and
means for controlling the force of the blade against the web.
49. Apparatus according to Claim 48 wherein the apparatus further comprises one or more additional blades downstream from the first blade for working the polymer composition into the web and removing excess polymer composition from the surface of the web and from within the web.

50. Apparatus for controlled placement of a polymer composition into a porous web having a plurality of structural members comprising:
means for advancing a porous web;
means for applying a curable, shear-thinnable, polymer composition to one surface of the web;
5 means for shear thinning the polymer composition to substantially reduce its viscosity and for placing the reduced viscosity polymer composition into the porous web to form a thin film coating on at least some of the structural members within the web;
means for controlling the longitudinal tension of the porous web during shear thinning of said polymer composition into said web;
10 means for scraping the excess polymer composition from the surface of the web; and
means for curing the polymer composition within the porous web.

51. Apparatus as set forth in Claim 50 wherein longitudinal tension on the web is substantially released immediately prior to and during curing.

52. Apparatus as set forth in Claim 50, including means for controlling said shear thinning means to form an internal layer of polymer within said web positioned in a region extending through the web in a direction generally spaced from at least one major surface of said web.

53. A method of controlled placement of a curable, shear-thinnable, polymer composition into a porous web comprising:
applying longitudinal tension to the porous web;
20 applying a polymer composition onto a surface of the tensioned porous web; and
shear thinning the polymer composition sufficiently to reduce its viscosity and selectively placing the viscosity reduced polymer composition under pressure into the porous web.

54. The method of controlled placement according to Claim 53 further comprising:
distorting the porous web at the location of the shear thinning to facilitate entrance of the polymer composition into the web.

55. The method of controlled placement according to Claim 54 wherein the distorting comprises stretching.

56. The method of controlled placement according to Claim 55 wherein the stretching is by passage of the web under a roller rotating against the web so as to move the web past a localized area where the polymer composition is placed into the web.

57. The method of controlled placement according to Claim 53 wherein the web is moved in one direction

against a roller which rotates in the opposite direction, and a polymer is applied between the roller and the moving web.

58. The method of controlled placement according to Claim 53 further comprising passing the treated web through a pair of nip rolls under longitudinal tension and allowing the tension to be released upon exiting the nip rolls to permit the fibers of the porous web to separate from each other.

59. A method of controlled placement of a polymer composition into a porous web comprising:
shear thinning a polymer composition into a porous web to reduce the viscosity of the polymer composition so that the viscosity reduced polymer composition will be controllably placed within the porous web; and

distorting the porous web at a location of the shear thinning to facilitate entrance of the polymer composition into the web.

60. A method of controlled placement of a curable, shear-thinnable, polymer composition into a porous web comprising:

applying a polymer composition onto a surface of the porous web;

applying longitudinal tension to said porous web;

shear thinning the polymer composition to substantially reduce its viscosity and placing the shear thinned viscosity reduced polymer composition into the porous web to encapsulate at least some of the fibers of the porous web without substantially filling the interstitial spaces of the web.

61. The method of controlled placement according to Claim 60 further comprising:

distorting the porous web at a location of the shear thinning and placing to facilitate entrance of the polymer composition into the web.

62. The method of controlled placement according to Claim 61 wherein the distorting comprises stretching.

63. The method of controlled placement according to Claim 62 wherein the stretching is by passage of the web under a roller rotating against the web so as to move the web past a localized area where the polymer composition is placed into the web.

64. The method of controlled placement according to Claim 62 wherein the distorting by stretching is by passage of the web between a first roller and a second roller that is delivering the polymer composition onto the web.

65. The method of controlled placement according to Claim 64 wherein the distorting by stretching is by passage between rollers rotating in the same direction.

66. The method of controlled placement according to Claim 65 wherein the rollers rotate opposite to movement of the web past the localized area.

5 67. The method of controlled placement according to Claim 64 wherein the distorting by stretching is between first and second rollers at least one of which exhibits a gravure surface.

68. The method of controlled placement according to Claim 64 wherein the distorting by stretching is between first and second rollers at least one of which exhibits a smooth surface.

10 69. The method of controlled placement according to Claim 62 wherein the distorting by stretching is by passage of a tensioned web against a bar knife.

70. The method of controlled placement according to Claim 69 that, after the distorting by stretching under a bar knife, further comprises:
scraping the porous web with a scraper so as to scrape excess polymer composition off the surface of the web.

15 71. The method of controlled placement according to Claim 70 wherein the scraping is under pressure against a tensioned web so that further pressure is exerted against the polymer composition so as to again reduce its viscosity and again place it, under this further pressure, into the porous web.

20 72. The method of controlled placement according to Claim 71 wherein the pressured scraping simultaneously occurs at a plurality of locations on the tensioned web as it moves under tension past a like plurality of scrapers.

73. The method of controlled placement according to Claim 59 wherein the shear thinning and placing comprises:
first pressuring in a pressured application stage that delivers the polymer composition onto and into the porous web under pressure;
25 second pressuring in a pressured excess-removal stage that further pressures the polymer composition that is in and upon the porous web resulting from the first pressuring further into the web while removing excess polymer composition that is upon and in the web.

74. The method of controlled placement according to Claim 73 wherein the first pressuring comprises:
rolling the polymer composition onto and into the porous web under pressure;
and wherein the second pressuring comprises:
scraping the porous web with a scraper so as to exert pressure thereagainst while removing excess
polymer composition by action of scraping.

75. The method according to Claim 74, wherein the rolling is between two rollers rotating in the same
direction thereby stretching the web between the rollers simultaneously so that the polymer composition
is rolled onto and into the porous web under pressure.

76. A method of controlled placement according to Claim 53 wherein the porous web has a plurality of
structural elements with interstitial spaces therebetween and the polymer composition is selectively
placed to encapsulate at least some of the structural elements of the web leaving some of the interstitial
spaces open.

77. A method of controlled placement according to Claim 53 wherein the polymer composition is selectively
placed in an internal layer within said web positioned in a region extending through the web in a
direction generally spaced from at least one major surface of said web.

78. A method of controlled placement according to Claim 76 wherein the polymer composition is also
selectively placed in an internal layer within said web positioned in a region extending through the web
in a direction generally parallel to and spaced from at least one major surface of said web.

79. A method of controlled placement in accordance with Claim 60 wherein the shear thinning and placing
is controlled to also selectively place the polymer composition in an internal layer within said web
positioned in a region extending through the web in a direction generally spaced from at least one major
surface of said web.

80. A method of controlled placement in accordance with Claim 53 wherein said web has a plurality of
structural elements with interstitial spaces therebetween and said selective placing is encapsulation of
at least some of the structural elements of said web, leaving at least some of the interstitial spaces open.

81. A method of controlled placement according to Claim 53 wherein said porous web has a plurality of
structural elements with interstitial spaces therebetween and the polymer composition is selectively
placed as an internal layer within said web positioned in a region extending through the web in a
direction generally spaced from at least one major surface of said web.

82. A method of controlled placement according to Claim 81 wherein the polymer composition is also selectively placed to encapsulate at least some of the structural elements of the web.

83. A method according to Claim 53 wherein said porous web has a number of open cells and said polymer composition is selectively placed to line at least some of the individual cell walls leaving at least some of the cells open.

84. A method according to Claim 83 wherein the polymer composition is also selectively placed in an internal layer within said web positioned in a region extending through the web in a direction generally spaced from at least one major surface of said web.

85. A method of controlled placement according to Claim 53 wherein said shear thinning and placing includes urging one or more blades against the tensioned web and polymer composition.

86. A method of controlled placement according to Claim 85 including controlling the force of each blade against said moving web.

87. A method of controlled placement according to Claim 85 further comprising controlling the tension of the web as it passes each blade.

88. A method of controlled placement according to Claim 85 comprising controlling the temperature of each blade.

89. A method of controlled placement according to Claim 85 comprising controlling the entrance angle of the web and the exit angle of the web from each blade.

90. A method of controlled placement according to Claim 85 comprising controlling the resonance of each blade.

91. A method of controlled placement according to Claim 85 comprising the longitudinal tension of said moving web.

92. A method of controlled placement according to Claim 85 further comprising the step of applying a transverse force to said web after shear thinning and placing.

93. A method of controlling the placement of a polymer composition into a porous substrate having a matrix

of open cells therein comprising the steps of:

applying tension longitudinally to said substrate;

applying a curable polymer composition having a viscosity sufficient to line the walls of said cells to at least one surface of said substrate;

5 moving against said surface of the tensioned substrate at least one of a uniformly applied compressive force and a uniformly applied localized shear force to selectively distribute said composition within said substrate, at least partially individually lining cell walls of at least some of said cells with said composition, and leaving most of said cells open.

10 94. The method of Claim 93 wherein said polymer composition has a viscosity greater than about 5,000 and less than about 2,000,000 centipoise.

95. The method of Claim 94 wherein the substrate is subjected to conditions sufficient to cure the polymer composition in said substrate.

96. The method of Claim 95 wherein said curing is accomplished by heat.

97. The method of Claim 95 wherein said curing is accomplished by radiation.

15 98. A method for making a fluorochemical and silicone resin treated substrate having breathability, water resistance and rewashability comprising the successive steps of:

- 20 (a) impregnating a porous substrate having generally open cells therein, with a fluorochemical;
- (b) applying a curable silicone polymer composition and concurrently applying a transversely exerted localized compressive force against one surface of the substrate;
- (c) moving relative to said surface of the substrate a substantially rigid shearing means which exerts transversely applied localized shear forces against said surface and which wipes away exposed portions of silicone polymer composition on said surface, thereby forming an internal layer of silicone polymer composition; and
- (d) curing the silicone polymer composition in said substrate.

25 99. The method of Claim 98 wherein said fluorochemical impregnated substrate is both longitudinally and laterally tensioned.

100. The method of Claim 98 wherein said porous substrate is a leather.

101. The method of Claim 98 wherein said porous substrate is a porous paper.

102. The method of Claim 98 wherein said porous substrate is an open celled plastic.
103. The method of Claim 98 wherein said porous substrate is an open celled sheet structure.
104. The method of Claim 98 wherein said substrate is a synthetic leather.
105. The method of Claim 98 wherein said substrate comprises a layer of an open celled, porous, flexible
5 material and a layer of a non-porous flexible material.
106. The method of Claim 98 wherein said fluorochemical impregnating is carried out by the steps
comprising:
 - (a) substantially completely saturating said substrate with a dispersion of a fluorochemical
containing composition in a carrier liquid;
 - 10 (b) compressing the saturated substrate to remove therefrom excess portions of said dispersion; and
 - (c) heating said substrate to evaporate said carrier liquid therefrom.
107. A method of controlling the placement of a polymer composition into a porous web comprising the steps
of:
 - 15 (a) tensioning a flexible, porous web comprised of fibers having interstices therebetween, said web
having generally opposed surfaces,
 - (b) applying a curable polymer composition having a viscosity greater than about 1,000 centipoise
to at least one surface of said web and then:
 - (c) moving over and against said surface of the tensioned web at least one of a uniformly applied
localized shear force or a uniformly applied localized compressive force to:
 - 20 (1) distribute said composition generally uniformly within said web,
 - (2) at least partially individually encapsulate at least some of said fibers with said
composition, and
 - (3) leave at least some of said interstices open.
108. The method of Claim 107 wherein the web is subjected to conditions sufficient to cure said polymer
25 composition in said web.
109. The method of Claim 108 wherein said curing is accomplished by heat.
110. The method of Claim 109 wherein said curing is accomplished by radiation.

111. A method for making a fluorochemical and silicone resin treated web having breathability, water resistance and rewashability comprising the successive steps of:

- (a) substantially uniformly impregnating the fibers of a porous web with a fluorochemical;
- (b) tensioning said fluorochemical impregnated web while sequentially:

- 5 (1) first applying a curable silicone polymer composition to a surface of said web while applying a transversely exerted localized compressive force against said surface, and
- (2) moving a substantially rigid, shearing means which transversely exerts an applied, localized shear force against said surface of the web to remove exposed portions of said silicone polymer composition from said surface, thereby individually
- 10 encapsulating at least some of said fibers with said silicone polymer composition; and
- (c) curing the silicone polymer composition in the web.

112. The method of Claim 111 wherein said porous web is a woven fabric.

113. The method of Claim 111 wherein said porous web is a non-woven fabric.

114. The method of Claim 111 wherein said fibers are comprised of a synthetic polymer.

15 115. The method of Claim 114 wherein said synthetic polymer is selected from the group consisting of polyamides, polyolefins, polyesters, regenerated cellulose and cellulose acetate.

116. The method of Claim 111 wherein said fibers are comprised of natural fibers.

117. The method of Claim 116 wherein said natural fibers are selected from the group consisting of cotton, linen, wool and silk.

20 118. The method of Claim 111 wherein said fibers are comprised of a mixture of natural fibers and synthetic fibers.

119. The method of Claim 118 wherein said fibers are comprised of a blend of cotton fibers and polyester fibers.

25 120. The method of Claim 111 wherein said web is a laminate of a woven fabric and a porous, flexible, non-woven substrate.

121. The method of Claim 120 wherein said substrate comprises a non-woven fabric.

122. The method of Claim 111 wherein said fluorochemical impregnating is carried out by the steps comprising:

- (a) substantially completely saturating said web with a dispersion of a fluorochemical composition in a carrier liquid;
- (b) compressing the saturated web to remove therefrom excess portions of said dispersion; and
- (c) heating said web to evaporate said carrier liquid therefrom.

123. The method of Claim 122 wherein the fluorochemical impregnated web has a weight increase in the range of about 0.01 to about 5 weight percent of the weight of the untreated web.

124. The method of Claim 123 wherein the silicone polymer composition impregnated web has a weight increase in the range of about 5 to about 200 weight percent compared to the weight of the untreated web.

125. Apparatus as set forth in Claim 2 wherein said polymer composition includes an additive and at least some of said additive is selectively placed on the surface of the encapsulated structural elements.

126. Apparatus is set forth in Claim 3 wherein said polymer composition includes an additive and at least some of said additive is placed on one or both surfaces of the internal layer.

127. Apparatus as set forth in Claim 4 wherein said polymer composition includes an additive and at least some of said additive is placed on the surface of the encapsulated structural elements and at least some of said additive is placed on one or both surfaces of the internal layer.

128. Apparatus as set forth in Claim 1 wherein said polymer composition includes an additive and at least some of said additive is selectively placed on one or both surfaces of said web.

129. A method of controlled placement as set forth in Claim 76 wherein the polymer composition includes an additive and at least some of said additive is selectively placed on the surface of the encapsulated structural elements.

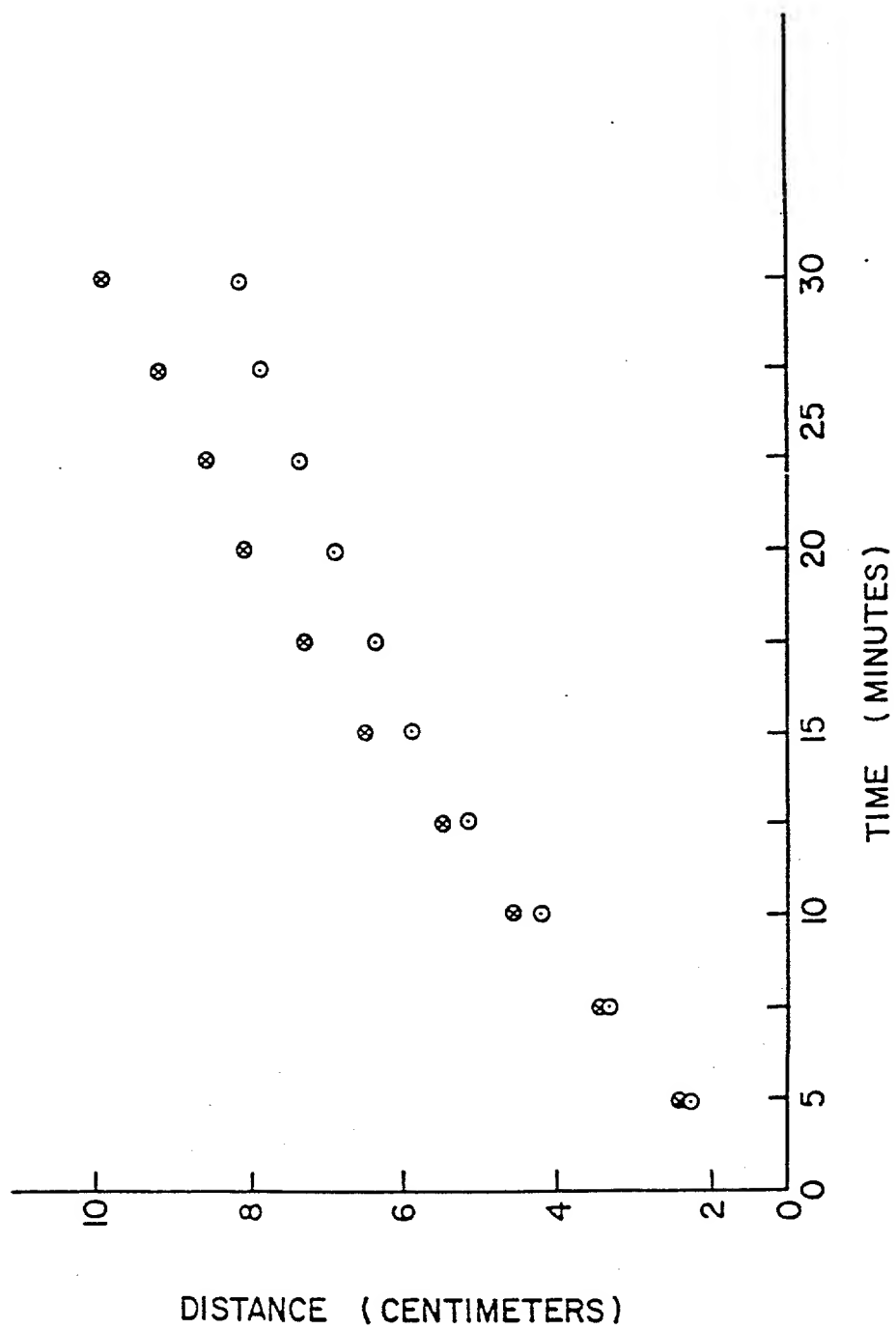
130. A method of controlled placement is set forth in Claim 77 wherein the polymer composition includes an additive and at least some of said additive is selectively placed on one or both surfaces of the internal layer.

131. A method of controlled placement as set forth in Claim 78 wherein the polymer composition includes an additive and at least some of said additive is placed on the surface of the encapsulated structural

elements and at least some of said additive is placed on one or both surfaces of the internal layer.

132. A method of controlled placement as set forth in Claim 53 wherein said polymer composition includes an additive and at least some of said additive is selectively placed on one or both surfaces of said web.

FIG. 1



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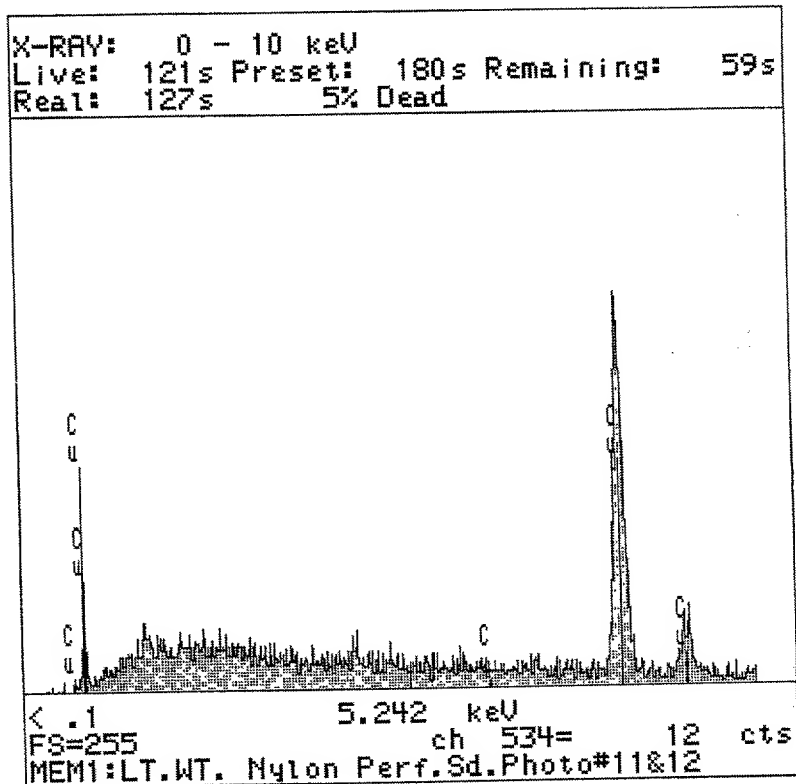


FIG. 15i

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of: J. Michael Caldwell)
Serial No.: Unassigned)
Filed: November 3, 1997)
Title: Methods and Apparatus)
for Controlled Placement of)
a Polymer Composition Into)
a Web)
File No.: 97-020)

Examiner:

Art Unit:

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APPOINTMENT OF NEW
POWER OF ATTORNEY**

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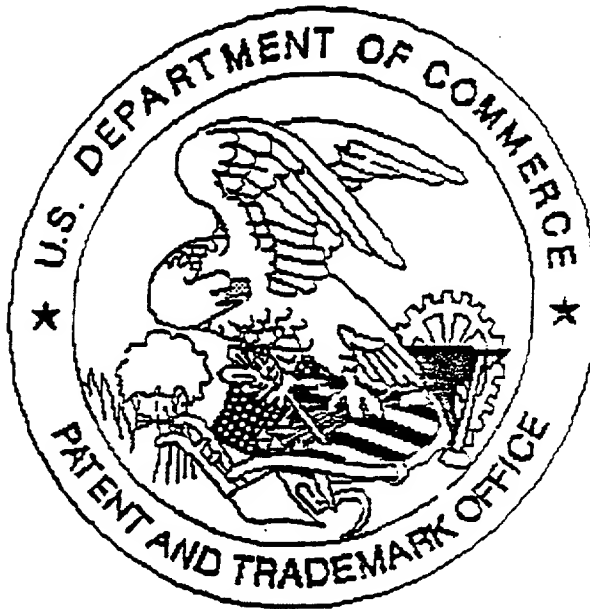
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